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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: REFINING ZINC SULPHIDE ORES

(57) Abstract

Zinc values are recovered from zinc sulphide–containing raw material feed by a process which includes the steps of smelting the raw material in the presence of a carbonaceous reductant to substantially reduce the zinc sulphide to metallic zinc, and to vaporize the zinc, thereby producing furnace gases containing zinc vapour and sulphur dioxide; and contacting the furnace gases with free–oxygen containing gas to oxidize the zinc metal and to produce zinc oxide rich crude fume in said furnace gases. The crude fume is separated from the furnace gases and collected and then mixed with concentrated aqueous ammonia/carbon dioxide solution, having a stoichiometric excess of ammonia, to produce a zinc–bearing leach liquor and to leave a solid residue. The leach liquor is separated from the residue, and ammonia then is stripped from the leach liquor to precipitate basic zinc carbonate and to leave a stripped leach liquor. The stripped leach liquor is separated from the basic zinc carbonate, and the latter is calcined to produce a purified zinc oxide product.

REFINING ZINC SULPHIDE ORES

This invention relates to a process for the metallurgical processing of suitable zinc sulphide-containing material. In one form, the process provides for the production of zinc oxide as an end product. In another form, the process

5   includes electrolytic refining for the production of zinc metal in which zinc oxide is produced for use as an intermediate for such production.

The invention has application in the processing of feed material comprising concentrates of zinc sulphide. However, the invention also is applicable to the processing of zinc sulphide ores, subject to their availability at a sufficiently high

10   grade for economic recovery through direct smelting. The invention also enables the separation and recovery of other metal values from the feed material, such as lead, silver, and cadmium usually present in zinc sulphide ores and concentrates.

The principal source of suitable feed material is zinc sulphide ores. In general, zinc sulphide ores are concentrated at or near the minesite, with flotation

15   the usual method. The concentration can be to provide a single, mixed metal, bulk concentrate containing most of the zinc mineral content of the ore, along with other mineral species. Alternatively, the concentration can produce at least two relatively clean concentrates, including a zinc rich concentrate and a second concentrate rich in another mineral species, usually lead. The production of a

20   single concentrate enables higher metal recoveries to concentrate, but can realise lower net smelter returns. Production of at least two concentrates realises greater net smelter returns, despite some contamination of each concentrate with unwanted mineral species.

Flotation, alone or in combination with other pre-concentration techniques,

25   necessitates crushed ore being ground to a particle size sufficient to liberate the zinc mineral species from the gangue minerals and from other mineral species. The size reduction required for this varies from one ore body to another, but it is not uncommon with sulphide ores having fine grained, intimately intermixed mineral species for it to be necessary to achieve 80% of ground particles less

30   than 20 microns or finer. Grinding to such fine sizes is costly in both capital and operating costs, while resultant high slimes levels interfere with flotation and necessitate desliming or selective flocculation. Moreover, where the zinc concentrate is processed for ultimate recovery of zinc metal by the electrolytic

process, fine particle sizes may give rise to a problem in such processing. Furthermore, tailings from finely ground ore generally are unsuited for high strength underground mine backfill requirements, which necessitates sourcing of additional fill material at added cost.

5   The zinc smelting industry is dominated by the Electrolytic Zinc ("EZ") process, developed in the early years of the twentieth century and first applied on a commercial scale in 1916. It is technically superior to the retort processes that it supplanted. The only other technology with a significant influence on the zinc smelting industry is the Imperial Smelting Process ("ISP"), which has higher costs

10   than the EZ process but which has the advantage of a greater flexibility in the raw materials it receives.

         The EZ process has a roasting stage, in which zinc sulphide-bearing mineral concentrate is heated to the point where the sulphur contained in the minerals reacts with atmospheric oxygen to form sulphur dioxide. Oxygen also

15   reacts with the metal ions remaining in the solid phase to form calcine comprising oxides of zinc, iron, lead, and other metals. The zinc contained in the calcine is dissolved in sulphuric acid, treated in several purification steps, and finally extracted from the acid solution by electrowinning.

         An ISP-based smelter uses a sinter plant to oxidise the zinc sulphide-

20   bearing concentrate and to fuse it to form sinter lumps of porous metal oxides. The sinter is placed in a sealed blast furnace in which the atmosphere contains substantial amounts of carbon monoxide. The carbon monoxide causes the conversion of zinc and lead oxides contained in the sinter to their metals, and the high temperatures causes the zinc to form a vapor. This vapor is carried from the

25   furnace in the off-gas and passes through a chamber wherein it is cooled rapidly by splashing with liquid lead at a considerably lower temperature. The zinc vapor is condensed and cooled by the lead, which passes out of the chamber through a weir. Subsequent cooling of the lead reduces the solubility of zinc in the lead and results in the separation of molten zinc as a layer floating on the circulating lead

30   stream and which can be removed and purified. The zinc produced by an ISP smelter is necessarily saturated with lead and is of lesser quality than that produced by an EZ smelter.

The principal difficulty with the EZ process is the fact that the electrowinning stage requires a very high purity electrolyte solution. The purification steps are expensive, and some elements such as manganese cannot practically be removed if present in concentrate in large amounts. Other elements, such as lead and copper, interfere with the roasting process if present above limited levels.

Miners faced with the choice of the sale of their zinc products to an EZ smelter or an ISP smelter frequently sacrifice metal recovery in order to produce concentrate meeting EZ feed specifications. With complex fine grained ores, separation of zinc, lead and silver is often difficult by conventional flotation methods and there can be significant loss of these valuable metals in tailings or as non-payable components, such as zinc in lead concentrates or lead and a large part of the silver contained in zinc concentrates. A bulk mixed concentrate suitable for an ISP smelter may achieve higher overall metal recoveries but financial returns to the mine are likely to be lower and market outlets are much more restricted.

The present invention provides an improved process for the recovery of zinc from zinc sulphide ore and/or concentrate. The invention is directed to providing a process for production of high grade zinc metal by production of zinc oxide product of a grade suitable for use as feed material for the production of metallic zinc by an electrolytic process; that is, by electrowinning. The process enables the disadvantages of conventional processes utilising preconcentration in the production of a zinc from ore to be obviated, while providing numerous practical benefits over the conventional route of preconcentration. At least in preferred forms, the present invention enables a more flexible method of smelting zinc sulphide-containing feed material and a means of maximising the value of individual metals payable to the mining operation. The process can tolerate greater concentrations of minor elements in the feed than can the EZ process.

Zinc oxide fume presently has limited use as raw material feed for zinc production by the electrolytic process due to the presence of impurities which are deleterious to that process, particularly halides. It is used more extensively as a concentrate feed replacement for pyrometallurgical processes such as the Imperial Smelting Process and the Retort Process, but usually such oxides are

derived from secondary materials at relatively low value, and not from primary ores.

The present invention provides a route for the efficient recovery and production of high quality zinc and by-product metals from complex ores using a unique combination of processing steps which include a fuming procedure and subsequent leaching and recovery steps to provide zinc oxide of a grade suitable for primary zinc recovery.

In the process of the present invention, zinc sulphide-containing feed material such as detailed above is subjected to a first stage, pyrometallurgical operation to generate crude zinc oxide fume product. The crude fume product then is subjected to a second stage, hydro-metallurgical operation to produce a high purity zinc oxide product and to separate other valuable metals such as lead and silver. The zinc oxide product then preferably is utilised, in a third stage of the process of the invention, as feed material in the production of metallic zinc by the electrolytic process. This can be a conventional electrolytic process for the electrowinning of metallic zinc, but preferably the zinc oxide product is used as feed for a highly simplified electrolytic process using a standard sulphate electrolyte.

In the first stage, the feed material is smelted in a high temperature furnace to oxidize sulphidic sulphur to sulphur dioxide, to volatize zinc into the vapour phase and to produce a molten slag containing the gangue minerals. The vaporised zinc is subsequently oxidized to a zinc oxide rich crude fume which is collected for further processing. The fume may contain lead and silver values but can be substantially free of gangue minerals such as iron, manganese and silica. The furnace may be a flash smelting shaft, a high temperature flame reactor, a shaft furnace, a kiln, or a slag bath reactor with either lance or tuyere injection. In one preferred approach, the feed material is smelted in a molten slag bath.

In the case of feed material smelted in a molten slag bath, the feed material is added to and dissolved in the slag and may require the addition of fluxing materials such as silica, lime, or iron compounds. The bath is agitated and heated by injecting air or oxygen-enriched air into the slag, below or onto the top surface of the bath. Zinc sulphide in the feed material is decomposed to zinc

oxide in the slag and sulphur dioxide. The zinc oxide so produced is reduced to elemental zinc by carbonaceous reductant charged to the slag whereby metallic zinc is volatilized from the bath. The resultant zinc vapor is oxidised in the gas phase above the top surface of the bath to form zinc oxide fume which is
5   removed from the furnace with sulphur dioxide and other combustion products in smelter gases. The fume is separated from the gases as a crude fume product.

In the second stage of the process, the crude fume product is leached in a concentrated aqueous solution of ammonia and carbon dioxide having a stoichoimetric excess of ammonia, that is, an ammonia/ammonium carbonate
10   (AAC) solution, to form a soluble zinc.ammonia.carbonate complex. Resultant leach solution then is treated to precipitate basic zinc carbonate product which is able to be recovered and calcined to provide a purified zinc oxide product. However, as detailed later herein, it is highly desirable that, before the AAC leach, the crude fume product is treated to remove sulphate.

15   The purified zinc oxide product produced by the second stage preferably is used in the electrolytic process for the production of metallic zinc. The zinc oxide can be utilised in the circuit of a conventional electrolytic process. However, it preferably is used in a modified electrolytic process as disclosed herein.

The present invention facilitates attainment of, or provides, significant
20   practical benefits and addresses significant difficulties associated with the currently employed technologies used in the main stream production of zinc by the electrolytic process. These include the following:

(a)   The invention enables high metal recoveries for each of zinc, lead and silver. This is achievable at both the mine and refinery and applies particularly
25   where the feed material is ore, rather than a concentrate, such that the loss of metal values in flotation failings is avoided.

(b)   The invention provides flexibility in relation to suitable feed materials. The feed material differs from the recycled residues, principally EAF dust, with which disclosures of the above-detailed patents of Peters and Keegel are concerned, in
30   that the feed material is either zinc sulphide ore or zinc sulphide concentrate. However, beyond this, the invention is flexible in relation to the mineral species in which the metal values are present, the relative amounts and mineral species of

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the gangue constituents, and the fineness and complexity of dissemination of the mineral species.

(c)   The process of the invention is able to be operated with a high level of environmental acceptability.   Substantially all wastes are able to remain at the mine/smelter site, in a slag suitable for use as land-fill, such as for mine backfill. Also, substantially no waste is produced in the leaching and electrowinning stages, since outputs other than the respective end products of zinc oxide and metallic zinc comprise by-products amendable to conventional processing. This particularly addresses the issue of iron residues in current electrolytic zinc technology.

In part, the present invention utilises technology known in other contexts. Thus, in a paper by Wendt, W.J. "Ammonia: ammonia carbonate leaching of zinc ores", Eng. Min. J. 154(9), September, 1953, 84-90, the process steps of the second stage of the present invention are proposed as a potential new process. Also, in US patent 4071357 issued on 31 July 1978 to Peters, there is disclosed the use of similar steps in the recovery of zinc.   Additionally, in U.S. patent 5538532 to Keegel, Jr., there is proposed a two-stage process for the recovery of zinc and other metals from electric arc furnace (EAF) dust. The first stage of the Keegel process involves roasting the EAF dust in a reducing furnace to vaporize, and to re-oxidize in the furnace, the cadmium, zinc, and lead, and to leave a residual sinter mass containing iron. The second stage of the Keegel process provides for an AAC leach and treatment for separation of cadmium, zinc and lead values.

In the case of the disclosure of Wendt, its context is different principally in that the zinc ores, specifically low grade oxidised zinc ores, are directly subjected to leaching by concentrated ammonia/carbon dioxide solution. Also, initial leaching of the ores is by grinding in the leach solution to minus 20 mesh, generating about 20% of minus 325 mesh material. After this initial leaching, the resultant solids are filtered to provide minus 325 mesh and plus 325 fractions, with each fraction then further leached. Zinc recovery, following the leaching, precipitation of zinc carbonate and its calcining, is indicated as over 95%. However, relatively fine grinding is necessary for this. Also, economical operation necessitates high zinc recovery being made in the smallest possible volume of

rich solution, although the solution volume needs to accommodate the presence of a high proportion of gangue minerals such as silica. Additionally, relatively lengthy leaching times are required.

The context of the disclosure of Peters is different in that it is concerned with recovery of zinc from EAF dust. The treatment of EAF dust, a material listed as being a hazardous waste, is to recover a substantial proportion of the zinc in the EAF solids feed. Such proportion is indicated by Example 1 of Peters to be about 55%, with the substantial balance of the zinc remaining in the form of zinc ferrite in a residue remaining after leaching the EAF dust with a concentrated solution of ammonia and carbon dioxide. Also, that residue retains about 95% of the lead and about 57% of the cadmium, the principal elements which resulted in EAF dust being listed as a hazardous waste. Peters indicates that some further zinc can be recovered by leaching the residue with acetic acid. However, there is no suggestion that the hazardous nature of EAF dust is not also substantially exhibited by the residue. Indeed, the residue, while reduced in weight relative to the EAF dust from which it is derived, is increased in lead content and retains a significant content of cadmium. As a result of this, and because of the low recovery of zinc, the procedure is not practical as proposed.

The process of Keegel also is applicable to EAF dusts. As indicated in USP 5538532, this material is composed mainly of oxides of iron, zinc, lead, tin, cadmium, chromium, manganese, nickel, copper and molybdenum; while silica, lime and alumina may be present. The process of Keegel is applicable to other materials comprising dusts generated in steel production, recycling of scrap metal and other metallurgical operations, including neutral leach residues, foundry and blast furnace dust, recovered metal powders and metallic ores. However, like the other materials specified, the ores do not include sulphide ores since the Keegel process does not take sulphur into consideration and, as is evident from USP 5538532, the process will not work for the recovery of zinc from a zinc sulphide ore or concentrate. This is the case where the end product is to be zinc oxide, but it is even more clearly the case where the end product is to be metallic zinc produced by electrolysis.

In the process of the present invention, the smelting may be conducted in a top-submerged lancing reactor system having a reactor vessel containing the

slag bath, and at least one top-submerged lance by which oxygen-containing gas is injected into the slag. Alternatively, the smelting may be in a similar reactor system but providing for top blowing rather than top-submerged injection. In a further alternative, the smelting may be conducted in a reactor containing the slag

5   bath, with the reactor having at least one side or bottom blowing tuyere by which the oxygen-containing gas is injected into the slag. In other alternatives, smelting may be conducted in a kiln such as a Waelz Kiln, in a shaft furnace or within a high temperature flame such as in a flash smelting furnace or flame cyclone reactor. Of these alternative systems, use of a top-submerged lancing reactor

10   system is preferred for a variety of reasons, including increased overall control of smelting conditions, avoidance of problems of blockage encountered with use of tuyeres and avoidance of the need for extensive feed preparation or presentation of a molten feed required in some of the other options.

For simplicity of description, the smelting required by the invention is

15   illustrated in the following by reference to a top-submerged lance reactor system. However, it again is pointed out that other furnace types can be used.

The zinc sulphide-containing feed material can comprise zinc concentrate. However, a zinc ore of a sufficient grade can be treated directly, rather than after pre-concentration, maximising the recovery of valuable metals.

20   The feed material does not require fine grinding and it may be charged to the slag bath as relatively coarse crushed material. The particle size can be set by the need to achieve dissolution of the feed material in the slag in a practical time since, as will be appreciated, finer particles will be dissolved at a faster rate than coarse lumps. However, fines smaller than two to three millimetres may

25   cause excessive dust carryover to fume and may therefore need to be limited, through the use of a pelletizer or some other agglomeration technique.

While the zinc sulphide-containing feed material can be charged to the slag bath in a wide variety of feed sizes, it is preferred that fines be charged separately from coarser and/or lump feed material, or agglomerated such as by

30   wetting and balling on a disc and fed with coarser material. This separation may not be necessary if the ratio of fines to coarser particles is sufficiently small. Agglomerated fines and coarser material can be charged through a suitable charging port of the reactor, such as via feed chute. However unagglomerated

fines may be injected into the slag bath, below the surface thereof, by a lance or tuyere whether this be the same lance or tuyere used for oxygen injection or another injector. With injection of fines, an upper limit on the proportion of fines to coarser and/or lump feed material may be necessary in some instances.

5   Moreover, control over the charging of fines will minimise their carryover with fume and smelting gases withdrawn from the reactor, thereby minimising the residue load in fume/gas separation and treatment of the fume in the second stage of the process.

The reductant preferably is coal in lump form. Where lump coal is used, it

10   preferably is added to the bath via a suitable charging port of the reactor which substantially precludes the egress of gases from the reactor. However, lump coal can be added via a lance and particulate coal can be used, if required. Also, other carbonaceous reductants can be used, although they generally are less efficient and/or are more costly than coal. The other reductants include, but are

15   not limited to, coke, coke breeze, natural gas, LPG and fuel oil. Such other reductants, or particulate coal reductant, can be supplied to the reactor by blowing, or by submerged injection into the slag via a lance or via a tuyere. The lance or tuyere for supplying the reductant may be the same as that providing for oxygen and fuel injection. Also, where a lance is used for oxygen and fuel

20   injection, a tuyere can be used for supplying reductant and, where a tuyere is used for oxygen injection, a lance can be used for supplying reductant. Where a lance or tuyere for oxygen injection also is used to inject reductant, the reductant may be entrained in a suitable carrier gas, such as nitrogen or air. In the latter case, the lance or tuyere most preferably has respective passages, such as

25   concentric passages, for separate flow therethrough of the oxygen and reductant which isolates them from each other at least until they are close to the discharge end of the lance or tuyere.

Some of the reductant may be burned to provide part of the energy requirement of the furnace. In this case, sufficient oxygen must be provided to

30   allow for this combustion and the oxidation of sulphur, iron and other compounds in the furnace. In the case of the zinc sulphide of the feed materials, the following reactions occur:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \quad\quad ....(1) \quad \text{or}$$

$$ZnS + O_2 \rightarrow Zn + SO_2, \quad\quad ....(2)$$

with similar reactions able to occur with other base or ferrous metal values present, such as lead, copper or iron. Iron oxide commonly is present in slags, either at the outset or by build-up in the slag from iron present in the feed material. Where iron oxide is present in the slag, it acts as an oxygen carrier which facilitates smelting by the reactions:

$$4FeO + O_2 \rightarrow 4FeO_{1.5} \quad\quad ....(3) \quad \text{and}$$

$$ZnS + 4FeO_{1.5} \rightarrow Zn + 4FeO + SO_2 \quad ....(4),$$

with similar reactions with other base metals, such as lead, also being facilitated.

The reductant and carbon monoxide generated during smelting further enhance smelting by the reactions:

$$ZnO + C \rightarrow Zn + CO \quad\quad ....(5),$$

$$ZnO + CO \rightarrow Zn + CO_2 \quad\quad ....(6),$$

with similar reactions for other base metals, such as lead. Also, the reductant gives rise to the reaction:

$$2FeO_{1.5} + C \rightarrow 2FeO + CO, \quad\quad ....(7),$$
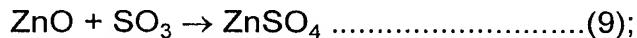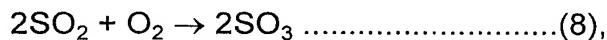
which results in regeneration of FeO as an oxygen carrier.

The free-oxygen containing gas can comprise air, oxygen or oxygen-enriched air.

The feed material need not only comprise sulphide. Thus, it may include sulphate and/or oxide but preferably with sulphide predominating. Depending on the feed material, the oxygen requirement for reactions (1) and (2) and similar reactions for other metal sulphides will vary with the total sulphide content, and for the requirement, if any, for combustion of part of the reductant as fuel.

Elemental zinc, generated in the slag by the reduction reactions, evolves as vapour from the slag. Similarly, other volatile metallic base metals or volatile base metal compounds in particular lead and lead compounds as well as silver and silver compounds, generated by smelting are evolved from the slag. The process most preferably is operated to optimise this evolution, while SO_2, CO, CO_2, H_2O and H_2 generated during smelting also are evolved. Free-oxygen containing gas, such as oxygen, air or oxygen-enriched air, is introduced into the

reactor, above the bath, to oxidise the vapours of any metal elements and any sulphur vapours to produce oxide fume, as required by the invention, and to prevent reversion of the elemental zinc in the vapour to sulphide. However, some sulphatizing of the zinc oxide can occur due to the reactions:

$$2SO_2 + O_2 \rightarrow 2SO_3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8),$$

$$ZnO + SO_3 \rightarrow ZnSO_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(9);$$

while some base metal sulphates, can be formed. The formation of lead sulphate is particularly likely and sulphate may be the principal way in which lead reports to the crude fume product.

The fume and smelting gases are extracted from the reactor via an off-take flue with the reactor sealed or operated at a reduced pressure above the bath to substantially prevent egress of fume and gases other than via the flue.

The smelting process may be divided into two stages. The first stage comprises a sulphur elimination stage under more oxidizing conditions and the second stage comprises a reduction stage wherein the zinc content of slag is reduced to a required final level by fuming. With low lead feed material to the first stage smelting operation, such as partially oxidised sulphidic ore or concentrate, the reducing conditions need not be as strong as with lead-containing feed material. However, with all feed materials, it is required that substantially all zinc is fumed with substantially all lead preferably recovered with the zinc fume. For this, the strength of the reducing conditions, controlled by the level of reductant addition, is one factor. Another factor is the temperature prevailing in the bath. The temperature required usually is in excess of about 1200°C up to about 1350°C..

Alternatively, it is also possible to operate the smelting process in three stages. The first stage comprises a sulphur elimination stage under more oxidizing conditions, the second stage being a reduction stage under such conditions as to produce a lead silver bullion and a zinc rich slag, and the third stage comprising a reduction stage wherein the zinc content of slag is reduced to the required final level by fuming.

It is also possible, where the concentration of lead is sufficiently high, to operate a two furnace system in such a fashion as to produce lead bullion in the first furnace. In this case, the slag passing to the second furnace is substantially

depleted in lead. The majority of the zinc reduction takes place in the second furnace. A third stage may be desirable to maximise both feed rate and zinc recovery.

5   With lead sulphide in the feed material, there is a tendency for it to evolve as lead sulphide. However, some of the lead sulphide is reduced to the metal, evolved and oxidised above the bath, principally to lead sulphate but with a proportion of lead oxide formed. The presence of lead sulphate in the crude fume is a problem, and, as detailed later herein, it therefore needs to be eliminated in a pre-treatment of the hydro-metallurgical stage. As indicated for a three stage 10   smelting process, lead can report in a lead-silver bullion, in which case a possibly minor proportion of the lead is evolved and oxidised.

The oxide fume and other evolved gases are extracted from the reactor of each stage via the off-take flue, and processed to recover a fume product. Preferably the fume and gases are cooled and passed to a filtration zone, such as 15   a baghouse, in which solid fume particles are retained and filtered from the gases.

The extracted gases, after removal of the fume particles, can be further treated for recovery of SO_2 for use in acid production.

The recovered fume product, comprising crude zinc oxide, or zinc oxide 20   with lead sulphate and other base metal oxides such as lead oxide, also can contain silver oxide. Depending on fume collection temperatures some sulphation can occur as well as the collection of halides and other minor elements such as selenium, arsenic, and germanium. The crude fume may also contain slag and feed carried over from the furnaces and such minor elements as cadmium and 25   bismuth. This crude fume product then is subjected to hydrometallurgical refinement according to the invention, for recovery of refined zinc oxide.

Where the extracted gases contain at least one of selenium, arsenic and germanium, it can be highly desirable to operate at a fume collection temperature which minimises the extent to which these elements report in the fume. With 30   cooling of the gases to baghouse temperatures in excess of about 200°C, the elements substantially will report in the fume. However, with higher collection temperatures permitted by electrostatic precipitators at about 400°C and, in particular, ceramic filters, the fume product can be substantially reduced in the

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content of selenium, arsenic and germanium, thereby substantially reducing the requirements for purification with respect to these elements at a later stage. This is particularly beneficial where high purity zinc oxide is to be produced for use in electrowinning metallic zinc by a simplified electrolytic process according to the invention.

With use of a single reactor, the smelting can proceed with a single lance or tuyere injecting oxygen-containing gas into the slag to give rise to closely adjacent regions in one of which zinc oxide is taken into the slag and the other in which the oxide is reduced to the metal and evolved. This is facilitated by use of lump coal which floats on the slag. Alternatively, the reactor may utilize two lances or tuyeres operating in respective regions of the bath, one providing for less strongly reducing conditions than the other. The less strongly reducing conditions favouring the smelting to zinc oxide with its take-up in the slag, while the more strongly reducing conditions result in reduction of the zinc oxide to metal vapour. In a further alternative, enabling use of a single lance or tuyere, these respective reducing conditions can be generated in successive periods of smelting, with some fume generated in the first period but most generated in the second period. However, use of two reactors can be beneficial to allow continuous operation. Less strongly reducing conditions can be generated in one reactor, with the zinc oxide-containing slag passing, such as via a launder, to the second reactor in which more strongly reducing conditions are generated.

In the hydrometallurgical stage of the process, the recovered fume product is leached in a concentrated aqueous solution of ammonia and carbon dioxide, having a stoichiometric excess of ammonia. The leach solution, effectively of ammonia/ammonium carbonate (AAC), takes substantially all of the zinc oxide into solution, but only minor amounts of lead and silver which predominantly remain in the leach residue. Oxides of some other metals present in the fume product also are taken into solution, while sulphate and halide ions also can be taken into solution. Other metals can be present in the fume, depending on the volatility of these elements or their compounds present in the feed material subjected to smelting, such as cadmium, arsenic, germanium and selenium. Also, a degree of feed material and carbon dust or slag can carryover into the fume, and thus introduce iron, manganese, copper, nickel, and cobalt, as well as other

gangue components such as silica, alumina, lime and magnesia into the leach solution. Of these copper, nickel, cobalt and cadmium are soluble in the leach solution together with traces of iron.

The fume product has a very fine particle size, in contrast to the major part
5   of the ground feed proposed in the paper by Wendt, where about 80% of the feed is greater than 325 mesh. As a consequence, the residence time for leaching is substantially reduced in the process of this invention. In general, a leaching time of 30 minutes or less is sufficient, compared with the several hours required by Peters for similarly fine EAF dust, and up to 48 hours indicated by Wendt for
10 substantially full dissolution of zinc oxide from oxidised ores.

To maximise the capacity of the AAC leach solution to disslove zinc, the solution preferably has about 100g/l of carbon dioxide or higher, and may be substantially saturated with respect to carbon dioxide. The stoichiometric excess of ammonia may be to provide a concentration of about 120g/l or higher of
15 ammonia for a solution having 100g/l or higher of carbon dioxide. In general, the excess of ammonia preferably is such that the ratio of moles of ammonia to moles of carbon dioxide is in excess of 3:1.

The rate of leaching, and the load of zinc oxide (and other oxides) able to be taken into solution by the leach solution, increases with the concentration of
20 ammonia and carbon dioxide. A substantially saturated leach solution is able to take into solution in excess of 150g/l of zinc as the oxide, although this loading will vary with the extent of other oxides taken into solution as well as the extent of sulphate and halides taken into solution. The pregnant solution resulting from leaching has a substantially depressed boiling point, necessitating leaching being
25 conducted below about 60°C unless conducted under pressure. However, while heating is preferred, excessive heating results in an undesirable level of evolution of ammonia and carbon dioxide, limiting the capacity of the solution to dissolve zinc and risking premature precipitation of zinc from solution. Heating most preferably is not at a temperature greater than is necessary for energy
30 minimization and for maximizing leaching rates.

Following leaching of the fume product, the pregnant solution is filtered to separate the solution from the residue. Filtering also separates with the residue any carbon dust particles from reductant and/or fuel, as well as particles of slag

and sulphide feed material, which are entrained in the fume and evolved gases extracted from the reactor in the first stage smelting operation. However, whereas the process of Peters results in a substantial zinc-rich residue remaining after the ammonia/carbon dioxide leach, due in part to zinc and possibly other base metals being present as ferrite, there is substantially less potential for ferrites to be a problem in the present invention. Thus, while a small amount of iron oxide may be present in the fume product, it will be in the form of slag particles separate from the zinc oxide and there seems to be little tendency for ferrites to be present in the fume product. Thus, the residue obtained with the process of the invention is low in zinc, and can substantially comprise a lead residue containing most of the silver content of the fume product, and insolubles such as slag and ore particles carried over with the fume.

It has been found that lead contained in the leach residue essentially has been converted to lead carbonate and that the sulphate ions are transferred to the pregnant leach solution. The lead carbonate contained in the leach residues can be readily reduced to metal by known methods, such as the use of a short rotary furnace, without any sulphur emissions. Any residual zinc values contained in the leach residues will report to the lead reduction furnace slag and may be recycled to the primary smelting stage for recovery into crude fume from the smelting operation.

The pregnant leach solution, after filtering to remove solids, then is treated for recovery of zinc values. For this, the pregnant solution preferably is stripped of ammonia and some carbon dioxide to give rise to precipitation of zinc as its basic carbonate. The precipitate is recovered, and then calcined to produce refined zinc oxide product.

The stripping of ammonia from the pregnant solution is effected by heating the solution to drive off the ammonia and thereby remove its stoichiometric excess. The heating may be by application of external heat energy to a vessel containing the solution, to raise the solution to its boiling point. However, this gives rise to complications of fouling heat transfer surfaces by precipitated basic zinc carbonate. Preferably heating is by direct steam injection in which ammonia is removed into the vapour stream. The steam stripping preferably is by a multi-stage, counter-current operation in which the pregnant solution passes through a

series of vessels, with fresh steam injected into the last of the vessels and passing in turn to the others. The vessels may comprise plate columns, such as of the bubble cap form, or packed columns. However, as the load of zinc in the leach solution and, hence the quantity of precipitate, is relatively high and can

5   cause blockage of the columns, the vessels preferably are agitated tanks fitted with steam spargers.

The ammonia and carbon dioxide stripped from the solution during precipitation of the basic zinc carbonate, together with the carbon dioxide in gases from calcining the basic zinc carbonate, can be recovered in a condenser-

10   absorber to regenerate leachate. Thus leaching reagents can be almost fully recycled and the major net process input is steam. Consequently integration with the smelting/fuming process is a major advantage of this invention since that part of the process will generate more than sufficient steam for the hydrometallurgical process.

15   Stripping of the pregnant leach solution enables substantially complete precipitation of zinc, substantially as its basic carbonate. This precipitation can be relatively selective, such that co-precipitation of some impurity elements such as halogens can be low. On completion of the stripping, the precipitate is recovered by filtering, washed on the filter and then is able to be calcined to provide high

20   purity zinc oxide product.

The residual solution may be recycled, after cooling, to the condenser/absorber to reconstitute leachate solution or may be totally or partially discarded from the circuit to provide an outlet for halides and any other soluble elements such as sodium and potassium.

25   The calcining step may be undertaken in any suitable calcining vessel, while the calcining temperature can be at any economically suitable temperature for decomposition of the basic carbonate, such as from 250°C to 600°C.

In order to further refine the purity of the zinc oxide it is possible to process the pregnant leach solution prior to steam stripping by the deliberate addition of

30   ferrous iron in soluble form to the solution, such as ferrous sulphate, during the final stages of leaching with aeration to cause oxidation of the iron and precipitation of hydrated iron oxides. This causes the separation by co-

precipitation of impurity elements such as arsenic, antimony, germanium and selenium.

Secondly, the filtered pregnant solution may be treated with zinc dust to cause those metals lower than zinc in the electrochemical series such as lead, cadmium, copper, nickel and cobalt, to be displaced from solution. A stoichiometric excess of zinc dust, relative to the metals to be displaced is preferred for this operation. The efficiency of this cementation separation can be higher in the filtered pregnant solution than in acid solutions.

As indicated, the smelting of the zinc sulphide-containing feed material to generate the crude fume product also generates sulphur dioxide which results in the formation of sulphates in the fume. The sulphate formation is predominantly associated with lead present in the fume. Some sulphide, again predominantly associated with lead, also can be present in the crude fume product. However, sulphur in that product usually is substantially present as sulphate.

In the process of Keegel disclosed in USP 5538532, a crude fume product is subjected to a second stage hydrometallurgical leach refinement, based on use of an AAC leach solution. In that refinement, recovery and recycling of ammonia and carbon dioxide, for regeneration of the AAC leach solution, is of considerable importance to economic operation. However, in contrast to oxidic feed materials such as EAF dust used in the Keegel process, similar operation with the sulphidic feed material required by the present invention results either in a zinc oxide end product contaminated by zinc sulphate or the need to recover carbon dioxide which contains sulphur dioxide.

Lead in the crude fume product of the present invention is precipitated as carbonate during the AAC leach, whether the lead is present as oxide or sulphate. However, with lead sulphate or other sulphate, it is found that sulphate ions will report in the pregnant AAC leach solution and to give rise to two undesirable results. The sulphate accummulates in the AAC solution circuit and reduces the capacity of the AAC solution to dissolve zinc, by locking-up ammonia as ammonium sulphate. It also means that ammonia cannot be fully recovered by the steam stripping operation and further treatment of any discard solution as an outlet for impurities will be necessary to recover ammonia. Additionally, basic zinc sulphate is co-precipitated with the basic zinc carbonate. Within the normal

calcining range of the basic zinc carbonate, basic zinc sulphate will not be decomposed and will be retained within and degrade the calcined zinc oxide product. The zinc content of the zinc oxide product can, for example, be reduced from about 80% to about 72% as a result of the presence of sulphate. For efficient decomposition of the sulphate content the calcining temperature would need to be increased to about 750°C. However, the product gases from such a calcining operation would contain sulphur dioxide which must be separated if carbon dioxide is to be recovered and recycled. The higher temperature calcination and presence of sulphur dioxide are complications which are best avoided by removing sulphate from the raw fume prior to AAC leaching.

We initially explored the possibility of removal of sulphate from stripped AAC solution by the addition of lime to precipitate gypsum. This precipitation released ammonia associated with the dissolved sulphate and consequently allowed recovery of this ammonia by steam stripping. The procedure provided a sulphate outlet but did not eliminate the effects indicated above of sulphate in the AAC circuit. Also, the lime treatment removed residual carbonate from the solution, due to precipitation of calcium carbonate before calcium sulphate, necessitating additional carbon dioxide input to the circuit. Moreover, even with such controlled removal of sulphate from recirculating leach solution by lime addition, necessarily conducted after the basic zinc carbonate precipitation stage, the zinc content of the product zinc oxide still can be reduced from about 80 wt% to about 72 wt% due to co-precipitated zinc sulphate.

We have found that the problems presented by sulphate can be overcome by a suitable pre-treatment of the crude fume product. In this, the crude fume product is subjected to a suitable aqueous wash, prior to the AAC solution leach, by use of a carbonate wash solution. The preferred wash solution is based on an alkali metal carbonate, preferably sodium carbonate. However, it also is possible to use an ammonium carbonate solution. With, for example, a soda ash pre-wash treatment, the following reactions occur:

$$PbSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + PbCO_3 \dots\dots\dots\dots (10),$$
$$ZnSO_4 + Na_2CO_3 \rightarrow NaSO_4 + ZnCO_3 \dots\dots\dots\dots (11).$$
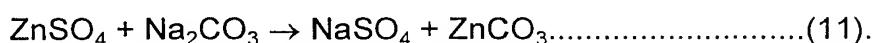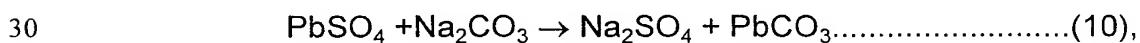
These conversions are able to proceed since each of lead and zinc carbonate is far less soluble than the respective sulphate. Resultant carbonate precipitate and the balance of the fume product are removed from the sulphate solution and rinsed, and the filtered solids then subjected to the AAC leach.

5   To maximise the efficiency of sulphate removal by the carbonate pre-washing of the crude fume product, a slight excess of carbonate beyond the stoichiometric requirement for removal of all sulphate is highly desirable. The excess may be up to or higher than 10% more than the stoichiometric amount, such up to 20% more than that amount. Removal of up to about 95% of all

10   sulphur, calculated as sulphate, has been found to be possible, with higher levels of removal being prevented by some sulphur being present as sulphide.

The carbonate pre-wash is found to result in negligible amounts of zinc and lead being taken into the wash solution, such as less than 0.01wt% based on solution analysis. Importantly, the carbonate pre-wash is found also to serve to

15   separate halides in a similar manner. Fume and washed fume analysis have shown 75 to 80% chlorine removal and 85 to 90% fluorine removal. The lower chlorine removal may be attributable to part of the chlorine being bound as highly insoluble silver chloride and will depend on relative levels of silver and chlorine present in the fume. Preliminary testwork has also indicated that the pre-wash

20   can remove at least 30 to 50% of thallium present in the crude fume product. Also, some removal of arsenic, such as at least up to 10% can be achieved.

As a result of pre-washing, higher zinc concentrations in the AAC leach solution are possible, a high grade zinc oxide at close to 80% zinc content can be produced, and recovery and recycle of ammonia is simplified.

25   As indicated, pre-washing of the crude fume product with ammonium carbonate is possible. This is more compatible with the AAC solution leach, as the ammonia can be substantially fully recovered using the same condensation and absorption equipment, whereas some loss of alkali metal from its pre-wash will occur. However, there is a greater risk of zinc extraction during pre-wash with

30   the use of an ammonium carbonate solution, while the efficiency of sulphate removal can be less than with an alkali metal carbonate such as soda ash.

In practice, a pre-wash solution preferably has a minimum excess of carbonate consistent with minimising bleed losses. With soda ash, as is preferred,

an excess of less than 15% above the stoichiometric requirement, such as an excess of about 10%, can be suitable. In the case for example of use of soda ash, the resulting sodium sulphate solution may be treated with lime to precipitate gypsum and generate a caustic soda solution, while the latter solution readily can

5   absorb carbon dioxide to reform the pre-wash soda ash solution. Some bleed of solution will be necessary to provide an outlet for halides, although this will result in a loss of sodium requiring a compensating input of fresh soda ash.

The high purity zinc oxide product which can be produced by this invention presents a feed to the electrolytic zinc process which essentially is able to

10   generate no residues. Consequently electrolytic refineries will be able to avoid major environmental difficulties associated with the disposal of iron residues such as jarosite or goethite.

Zinc rich oxide fumes have not been favoured as a feed to electrolytic zinc refineries largely because of the presence of halides and other minor impurities

15   which are particularly deleterious to the electrolytic process. The latter include volatile elements such as arsenic, antimony, germanium and selenium. In addition high levels of lead are not favoured as the resulting lead sulphate leach residues are not readily marketable as a raw material feed to lead smelters and consequently have relatively low value or the lead contaminates iron residues for

20   acceptable disposal, if the fume is used for iron precipitation. Advantages for the present invention are the separation of zinc and lead, the separation of halides, and the opportunity to separate the full range of deleterious minor elements in or before the second stage leaching operation to present a high purity zinc oxide for electrowinning of metallic zinc. A substantial proportion of halides present in the

25   initial feed material to the first stage smelting operation can be decomposed and eliminated in smelter gases. Halides which may be captured in the crude fume product may be minimised by operating at elevated fume collection temperatures but, in any event, are able to be finally removed in both the pre-washing and the AAC leaching operation.

30   The process of this invention also recovers substantially all lead and silver values in a high grade carbonate residue from the fume leaching stage which may be readily reduced to a lead-silver bullion by known pyrometallurgical methods such as the use of a short rotary furnace. This may be integrated into

the total process whereby slag from lead reduction can be returned to the smelting stage to improve overall metal recoveries and provide for only one waste slag product. This avoids or substantially reduces by-product lead-silver residue production at the zinc refinery. These are usually low grade sulphate residues of marginal value, and represent a significant loss of value in the overall metal production process.

Alternatively if a smelting operation is used to directly produce a bullion at the first or second smelting stage, fume leach residues would be directly returned to the first smelting stage.

The high grade zinc oxide product may be agglomerated, such as by granulation, into a dust free form, for example, by using various binding agents such as zinc sulphate or sulphuric acid for transport to an electrolytic zinc refinery. This invention will significantly reduce the quantity of feed materials to be transported between mine and electrolytic refinery which is normally located close to sources of low-cost electric power.

Although a high grade zinc oxide may be supplied as a raw material to existing electrolytic zinc refineries and will enable considerable process simplifications, with cost and metal recovery improvements, a preferred embodiment of this invention would be to incorporate a dedicated zinc electrowinning stage in the overall process which may be located adjacent to, or separate from, the oxide production facilities. Such a dedicated electrowinning operation may be greatly simplified in comparison with conventional electrolytic zinc refineries. Firstly roasting and acid production facilities are not required. Complex leaching and iron separation processes are unnecessary and substantially all waste residues are eliminated. The processing steps may be confined to the use of facilities for a simple oxide leach in spent electrolyte, the electrolytic tankhouse, and cathode melting and ingot casting facilities. The highly simplified leaching facilities, with no or minimal purification requirements, will largely remove constraints on circulating solution volume and will permit operation of the electrolysis stage at higher zinc and lower acid concentrations than is normal practice. This will enable a significant improvement in deposition current efficiency with a reduction in electrical energy consumption as the single largest cost item for this process. Operation at higher temperature is also

possible with the lower acid concentrations, and this will reduce cell voltages for zinc electrodeposition and simplify solution cooling requirements.

The substantial absence of elements such as magnesium and manganese will allow for further increases in the zinc concentration of electrolyte and will
5   reduce operating cell voltages, again contributing to a reduction in electrical energy consumption.

The absence of manganese is likely to necessitate the use of titanium anodes in place of the conventional lead anodes at higher initial cost. However this will improve the quality of the zinc deposit by substantially eliminating lead as
10   the major cathode zinc impurity, and will substantially avoid the cost of reagents such as strontium carbonate which are used to minimize levels of lead in the cathode zinc. It will also substantially eliminate the operations of regular anode cleaning and cell de-sludging.

A possible flow sheet is shown in Figure 3 which essentially consists of
15   zinc oxide leaching, electrowinning, zinc cathode melting and ingot casting facilities. The flowsheet also includes an optional zinc dust purification stage and provision for bleeding a small portion of circuit solution through a basic zinc sulphate precipitation step to serve as an outlet for soluble impurities such as halides. An alternative approach would be to feed the bleed solution to an
20   evaporative crystallizer to produce a zinc sulphate by-product for sale. These solution purity control measures are additional to the impurity separation achieved in the AAC leaching of crude fume. They are included as a prudent safeguard for the electrowinning operation and may in fact be unnecessary.

Dross from cathode melting may be returned to the primary leach after
25   washing with sodium carbonate solution to separate chlorides, or it may be returned untreated to the smelting stage or to the subsequent crude fume pre-wash and leach. The option selected will depend on requirements for halide balance control.

The overall impact of a feed of high purity zinc oxide to a dedicated
30   electrolytic zinc refinery is a major reduction in capital and operating costs compared with conventional plants, improved metal quality and the elimination of environmental issues associated with the residues produced from conventional plants.

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The process of the invention enables operation with substantial environmental benefits. The products of the first stage smelting, in addition to generating fume and smelting and combustion gases, can be operated to provide a slag that will not leach heavy metals in quantities that may be damaging to the

5   environment. The slag is low in environmentally hazardous base metals. If the operation is conducted at a minesite the slag may be produced in a form suitable for mine fill. The slag is also free of sulphur, avoiding common problems with acid generation in mine tailings. The overall operation of the process of the invention can limit the production of solid wastes essentially to that slag, substantially

10   eliminating the production of iron and other leach residues from the electrolytic zinc process. Other deleterious elements in minor quantities, such as arsenic and thallium, can be produced in such a form that they can economically be rendered harmless, such as mixing with concrete that can be used to add strength to fill in underground mining processes.

15   The overall process of this invention, particularly if applied to the direct processing of ore, can greatly enhance the overall recovery of valuable metals. Performance is independent of mineral grain size, mineral type and complexity which often severely affects the effectiveness of metal recovery in physical separation processes such as flotation.

20   Subtantially complete separation of lead and zinc is achieved and cross contamination of metal products with consequent loss of value to the mineral producer is able to be avoided or substantially reduced. Similarly the substantial elimination of waste metal contamination in the electrolytic process and resulting residues virtually eliminates metal losses from that stage of the process.

25   Recovery of metal values from an ore resource can thus be greatly enhanced.

As with the present invention, the Keegel process of USP 5538532 proposes an integration of the production of zinc oxide product with electrolytic winning of zinc. However, in the Keegel process, this is limited to the use of neutral leach residue by-products of zinc electrowinning by zinc smelting plants

30   as feed material, in place of or additional to EAF dust. That is, the proposal is limited to the context of a conventional electrolytic process which utilises conventional calcine from a zinc smelting plant. Even in this context, there is no suggestion that the zinc oxide product of the Keegel process is suitable for use as

feed material, at least in part in place of conventional calcine in a conventional electrolytic process, let alone that it is possible to use the zinc oxide product as the sole source of zinc feed material for a dedicated electrolytic process for electrowinning of zinc.

As evident from the disclosure herein, the form of the present invention providing a three-stage operation producing metallic zinc by a dedicated electrolytic process has:

(a)   a first, pyrometallurgical stage which produces crude fume;

(b)   a second, hydrometallurgical stage for which the crude fume is the feed material and which separates lead and silver from zinc and produces zinc oxide product; and

(c)   a third, electrometallurgical stage for which the zinc oxide product is the feed material and which produces metallic zinc.

This vertical integration thus proceeds from zinc sulphide ore or concentrate through to zinc metal with the by-product production of lead bullion containing silver. In contrast to this vertical integration, the level of integration suggested by the teaching of Keegel is of:

(A)   a first process line comprising the EZ process, having:

(i)   a first pyrometallurgical stage in which zinc concentrate is roasted to evolve sulphur dioxide and leave solid calcine;

(ii)   a second, hydrometallurgical stage in which the calcine is leached to form a zinc sulphate rich solution which then is purified; and

(iii)   a third, electrometallurgical stage in which metallic zinc is recovered by electrolysis from the purified solution; and

(B)   a second process line comprising the Keegel process, having:

(i)   a first pyrometallurgical stage in which zinc oxide containing material is heated to evolve vapour zinc and other metals, with the vapours then oxidized to form a fume;

(ii)   a second hydrometallurgical stage to which the fume is feed material and which produces zinc oxide product.

In processes (A) and (B), the respective pyrometallurgical stages are distinct, as are the respective hydrometallurgical duplication in facilities and costs. The only

integration is that the feed for the first stage of process (B) is by-product neutral residues from the second stage of process (A).

Reference now is made to the accompanying drawings, in which:

Figure 1 is an overall flow-chart for the process of the present invention;

5   Figure 2 is a flow-chart of the second stage of the process of Figure 1; and

Figure 3 is a flow-chart of the third stage of Figure 1.

The process depicted in Figure 1 is suited for the treatment of zinc sulphide ore of a grade suitable for smelting. However, the flow-chart readily is able to be used with other zinc sulphide-containing feed materials detailed herein.

10   After primary crushing, the zinc sulphide ore passes to a secondary crusher 10, if necessary via an ore bin 12. The ore from crusher 12 passes to feeder bin 14, with the stockpile at 16 providing surge capacity. From bin 14, the ore is passed to a mixer 18, such as a pugmill or pelletizer, in which it is mixed with flux, such as silica from bin 20 and/or limestone from bin 22, and with coal

15   from bin 24. From mixer 18, the ore mixture passes to a first top-submerged lancing reactor 26, in which it is melted.

Reactor 26 is a refractory-lined steel vessel 28 containing a suitable molten slag bath 30, preferably of an iron oxide containing slag. The reactor 26 has a top-submerged lance 32 having its lower, discharge end submerged in the slag.

20   Oxygen from source 34 is able to be mixed with air and supplied to lance 32 under the action of blower 36. Feed mixture from mixer 18 is supplied to reactor 26, and is charged to the bath 30. Under turbulent smelting conditions in reactor 26, the ore is smelted under mildly reducing conditions causing sulphur elimination as SO_2, and the taking of zinc and lead values into the slag as the

25   oxide. A significant quantity of lead may be fumed as lead sulphide and a degree of reduction of the lead and zinc oxides can occur, with evolution of the respective metals and formation of lead sulphate. Silver follows the lead values in the absence of formation of a matte phase during the smelting. Resultant fume is oxidised above the slag, to provide crude oxide fume product. This product may

30   contain significant quantities of lead sulphate. The fume product, SO_2 and other smelting gases are drawn from reactor 26 via its flue 38 and is passed to waste heat boiler 40. Oxide containing slag is tapped from reactor 26, such as at

required intervals or continuously, and passed to a second reactor 26a which is similar to reactor 26.

In reactor 26a, the slag is subjected to further, similar top-submerged smelting, but under more strongly reducing conditions. Air or oxygen-enriched or nitrogen-enriched air is injected via lance 32a, into the slag bath 30a, with the supply of further air or oxygen-enriched air supplied to the reactor space above bath 30a. Coal from bin 42 is passed to mill 44 in which it is reduced to a suitable size. From mill 44, the coal is entrained in nitrogen or air in injector 45 from which it passes to lance 32a for injection into bath 30a.

In reactor 26a the zinc and lead oxides are reduced to the respective metal which are evolved from bath 30a. The metal vapours are oxidised above bath 30a to provide further crude zinc oxide fume product containing lead sulphate which product, with residual SO_2 and smelting gases, is extracted via flue 38a and passed to waste heat boiler 40. Slag with low levels of zinc and lead is tapped from reactor 26a, and passed to granulator 46 and then either passed to stockpile 48 or to ball mill 50 in which it is ground, for use such as mine fill. The broken outline from slag granulation system 46, and reactors 26 and 26a indicates the hygiene system ducting designed to carry fugitive metal fumes from these points to the hygiene system baghouse 51.

The respective fume/flue gases from reactors 26 and 26a are cooled sufficiently in boiler 40 (followed by water quenching if necessary) to enable the fume/flue gas to be passed to baghouses 52. A turbine/condenser system 53 preferably converts waste heat energy to electricity to power the oxygen plant, the air blowers and other items of electrical equipment used in the plant. Any excess electricity generated may be sold onto an electricity grid. However, it is possible to drive blowers directly from the steam produced in the smelters. In addition, some pass-out steam can be taken from the turbine for use in the ammonia/ammonium carbonate leach process described below.

At the baghouse 52, crude fume product is separated from the flue gases. The fume products then pass to holding bin 54, while the flue gases pass to a plant 56 for recovery of SO_2, such as for generation of sulphuric acid, and removal of volatile compounds or chemical elements such as mercury. The tail gases from the acid plant discharge via stack 57.

Zinc oxide fume product from bin 54 is passed to a leaching plant 58, shown in detail in Figure 2, for recovery of a purified zinc oxide product and to produce a silver-lead carbonate product. The zinc oxide product is passed to an electrolytic installation 60, shown in more detail in Figure 3, for the electrowinning

5   of high grade zinc metal. The silver-lead product is passed to a suitable furnace 62, such as a rotary furnace, in which it is smelted to recover lead-silver bullion. Slag generated in furnace 62 can be recycled, such as to the feed for furnace 26.

As shown in Figure 1, and in more detail in Figure 2, the zinc oxide fume product from bin 54 may pass to a pre-treatment unit 55 before passing to

10   leaching plant 58. In unit 55, the zinc oxide product is washed with an aqueous carbonate solution, such as of sodium carbonate. The washing causes metal values present in the oxide powder as sulphate to precipitate as the carbonate, while sulphate ions are taken into solution and discarded with the wash solution or are discarded as gypsum by precipitation with lime.

15   As shown in more detail in Figure 2, unit 55 has a vessel 55a in which the fume product is mixed with recycled and/or regenerated soda ash solution. In vessel 55a, metal values present as sulphate are converted to carbonate which precipitates, while sulphate ions are taken into and remain in solution. The mixture formed in vessel 55a is passed to thickener 55c from which overflow

20   sulphate containing solution passes to vessel 55d and solids pass to filter 55e. The solids, comprising the oxide component and other insolubles of the fume product, with the carbonate precipitate, are washed on filter 55e and then pass to leach tank 70.

In vessel 55d, the sulphate bearing solution is contacted with lime, to

25   precipitate gypsum which is separated as solids passing thickener 55f and retained and washed on filter 55g. The washed gypsum passes to a tailings dump or the like. Wash liquid from filter 55g and overflow from thickener 55f are passed to a carbonation tower 55h, in which the soda ash solution is regenerated. For this, carbon dioxide is passed to tower 55h from kiln 55i in which limestone is

30   heated to generate lime for use in vessel 55d.

As shown in Figure 2, the crude fume product received into bin 54 is passed, directly or via unit 55, to a leach tank 70 in which it is treated with a concentrated aqueous leach solution 72 of ammonium carbonate having a

stoichiometric excess of ammonia. The leach tank 70 may be a single tank or several tanks in series. The fume/solution mixture is agitated by stirrer 74. The zinc oxide is taken into solution as zinc ammonium carbonate complex, along with some impurity metals, such as cadmium, copper and nickel carried over with the fume in the smelting stage. After substantially all of the zinc has been complexed, the solution is passed to a thickener 76. Solids withdrawn from the thickener pass to a filter 78. Pregnant solution removed from thickener 76 and filtrate from filter 78 are recombined for further processing, while solids retained by filter 78 are washed by water added at 78a before being passed to the furnace 62 referred to in relation to Figure 1, for recovery of lead-silver bullion.

As shown in Figure 2, an optional purification step can be provided between tank 70 (or the last tank 70 of the series) and thickener 76. With this option, the solution from tank 70 is passed to a tank 75 in which it is treated with iron sulphate solution from line 75a and aeration by bottom injected air from line 75b. This iron treatment results in precipitation of ferric hydroxide, with co-precipitation of metals such as arsenic and germanium. The precipitate is removed by filter 78, and then passes with other filtered solids to furnace 62.

The recombined solution from thickener 76 and filter 78 preferably are purified in tank 80 by addition of zinc dust. Resultant cementation results in precipitation of metals lower than zinc in the electrochemical series, including cadmium, lead, copper, and nickel. The solution then is filtered by filter 82, to remove the precipitate, following which the solution is treated in a series of preferably four vessels (shown as 84a and 84b) of a multistage steam stripping system. The solution passes first to vessel 84a and then to vessel 84b. Steam via line 85 is injected into the base of vessel 84b and then is passed from vessel 84b and similarly through vessel 84a. The steam strips the excess ammonia from the solution, along with some carbon dioxide, with resultant precipitation of high purity basic zinc carbonate. The mixed gases issuing from vessel 84a are passed to condenser/absorber vessel 86 for use in regeneration of the initial leach solution for tank 70.

The stripped solution from vessel 84b is passed to the thickener 88, and the settled solids to filter 90 for recovery of the basic zinc carbonate. The carbonate is washed on filter 90 by water from line 90a and then is passed to an

indirectly fuel fired calcining kiln 92 to generate zinc oxide, with recovery of carbon dioxide. The recovered carbon dioxide is recycled for leach solution regeneration in condenser/absorber vessel 86, with make-up CO_2 and water also being provided to vessel 86.

5   Leach solution recovered from thickener 88 and filter 90 also are recycled, via cooling tower 94, to condenser/absorber vessel 86. However, filtrate from filter 90 and/or overflow from thickener 88 may be discarded to provide a bleed for halides as sodium or potassium salts.

The zinc oxide calcine product from kiln 92 passes to installation 60, as
10   shown in Figure 1 and in detail in Figure 3. However, if required, some or all of the high-purity zinc oxide can be recovered for direct sale.

As shown in Figure 3, the zinc oxide from calcining kiln 92 passes via a fume hopper 102 to a leach tank 100, which may be one of a series of such tanks. In tank 100, the zinc oxide is digested in part of spent electrolyte recycled
15   from electrolytic cells 104 used to produce cathode zinc. The latter is suitable for melting in furnace 106 for casting at 108 of high purity zinc ingots. However, if required, the cathode zinc can be used to provide zinc dust, at least in a quantity useable in the electrolytic refining circuit.

Part of the recycled spent electrolyte passes to cooling system 110 and is
20   returned to cells 104.

The bulk of the leach solution from tank 100, comprising a zinc sulphate solution on digestion of the zinc oxide and any recycled zinc dust, is passed to a clarifier 112. The overflow solution from clarifier 112 passes to cells 104, if required, via an optional purification step. The latter includes passing the zinc
25   sulphate solution to agitated tank 114 in which it is treated with zinc dust to precipitate minor impurity residuals such as copper and cadmium. The solution then passes to filter 116, and then to cells 104 via cooling system 110. The precipitate from filter 116 can comprise a copper-cadmium cement which can be recovered for sale.

30   The small quantity of residue from clarifier 112 is subjected to a strong acid leach in tank 115, using part of the recycled electrolyte and fresh acid if required for sulphate make-up. The acid solution and resultant residue are passed to filter 120, to separate the residue from the solution which is passed back to tank 100.

The residue, which will be a relatively minor quantity, can be returned to furnace 26a, but preferably to furnace 26, both shown in Figure 1.

A minor part of the solution of tank 100, resulting from digestion of zinc oxide, is passed to a two stage impurity level control system which, while requiring only a single vessel 124, has its stages represented as stage 1 and stage 2. In stage 1, the minor part of the solution is treated with zinc oxide from hopper 102, to precipitate basic zinc sulphate. In stage 2, lime is added via line 124a to precipitate residual amounts of zinc from solution as additional basic zinc sulphate. The solution then is passed to filter 126 which separates the precipitate. The liquid from filter 126 containing soluble impurities such as halides is discarded via line 126a, while the basic zinc sulphate precipitate is recycled to vessel 100.

EXAMPLE 1

A series of pilot plant runs were conducted to demonstrate the fuming step on both zinc sulphide ore and concentrate. While a two-stage top submerged injection system of a commercial plant would normally treat, in a reduction furnace, hot slag from an oxidation furnace, the pilot plant consisted only of a single furnace. Thus the reduction stage was demonstrated by treating slag from the oxidation furnace that had been cooled and crushed. The fuel consumption in the pilot plant reduction trials was therefore higher than would be the case in a system in which the reduction stage treated hot slag. As a result of the use of additional fuel, the air flow rate used for each unit of feed during the reduction trials was higher than would be the case in a commercial plant. The operating conditions of the reduction furnace are therefore an approximation of the operating conditions of a commercial plant.

The pilot runs consisted of 11 oxidation runs using low-grade zinc sulphide ore obtained from the 4-Level of the Lady Loretta mine in North West Queensland, three oxidation runs using high-grade ore from the mine's 6-Level, two oxidation runs using a bulk concentrate, and four reduction runs. Three of the reduction runs were undertaken using slag produced from the oxidation of the 4-Level ore. One of these was a batch reduction, in which ore was added to a slag under oxidising conditions to raise the zinc level to 5 to 6%, and then reducing

conditions were imposed. This oxidation and reduction cycle was repeated during the same test. The remaining reduction run used all the slag produced from the oxidation of the bulk concentrate and 6-Level ore. Table 1 gives average analyses for the oxidation runs; while Table 2 presents the average composition of the slag used in the reduction runs.

Table 1 - Average ore or concentrate feed composition for oxidation runs

Feed	Zinc	Lead	Silver	Iron	Sulphur	Silica	Alumina	Lime
4-Level ore	14.95%	10.68%	121 g/t	15.38%	23.33%	24.04%	4.42%	0.2%
6-Level ore	43.3%	3.12%	90 g/t	8.73%	29.0%	6.93%	3.2%	0.04%
Bulk con-centrate	26.3%	17.3%	185 g/t	13.0%	25.5%	8.2%	1.85%	0.35%

Table 2 – Average slag feed composition for reduction runs

Feed	Zinc	Lead	Silver	Iron	Sulphur	Silica	Alumina	Lime
4-Level ore	8.90%	0.30%	90 g/t	20.25%	4.45%	31.00%	6.10%	18.25%
6-Level ore & bulk con-centrate	11.0%	0.001%	60 g/t	25.5%	3.3%	25.5%	7.9%	10.6%

The average compositions of the slag and fume generated from the oxidation runs using 4-Level ore are presented in Table 3 which also gives the average composition of the ore. Table 3 includes the average composition of the slag and fume produced during the reduction runs using slag generated by oxidation smelting of 4-Level ore. However, it should be noted that the reduction runs were undertaken using only part of the slag generated during the oxidation runs. Consequently, the feed to the reduction process was not identical in composition to the average slag produced during the oxidation tests.

Table 3 – Average composition of 4-Level ore feed, slag and fume

	Ore	Oxidation slag	Oxidation fume	Indicative distribution to fume (%)	Reduction slag	Reduction fume	Indicative distribution to fume (%)
Zn (%)	14.95	8.04	33.0	57.2	1.41	63.5	85.33
Pb (%)	10.68	0.36	36.8	89.3	0.09	9.13	363.98
Fe (%)	15.38	19.2	0.39	0.7	21.9	0.15	0.08
S (%)	23.33	3.54	5.82	6.5	1.66	2.18	5.86
SiO$_2$ (%)	24.04	30.9	0.25	0.3	33.92	0.22	0.08
CaO (%)	0.20	18.31	0.10	-	19.4	0.05	0.03
Al$_2$O$_3$ (%)	4.42	6.13	0.05	9.0	7.20	0.05	0.10
Ag (g/t)	121	77	180	38.5	35	354	47.04
K (%)	1.65	1.93	0.57	9.0	2.03	0.69	4.17
C (%)	0.87	-	0.52	15.5	-	0.81	-
MgO (%)	0.59	2.40	0.01	0.4	4.16	0.02	0.11
BaO (g/t)	1920	2300	114	1.5	2500	79	0.41
As (g/t)	1280	160	4600	93.1	130	1350	100.91
Cu (g/t)	1360	2140	340	6.5	1800	370	2.36
F (g/t)	408	108	660	41.9	25	740	70.80
Cd (g/t)	275	9.2	950	89.5	-	200	-
Cl (g/t)	267	148	440	-	400	490	-
Na (g/t)	195	340	70	9.3	420	90	0.08
Co (g/t)	156	312	7.6	1.3	410	6.5	0.23
Mn (g/t)	124	245	7.9	1.7	326	4.7	0.21
Sb (g/t)	110	21	328	77.3	5.9	317	189.57
Cr (g/t)	67	1540	26	10.1	1720	37	0.57
Sn (g/t)	23	33	117	131.8	88	235	28.11
Tl (g/t)	40	3.2	122	79.0	0.4	42	251.16
Ge (g/t)	35	8.0	120	88.8	1.0	88	105.25
Se (g/t)	8.3	20.7	47	146.7	-	-	-
Ni (g/t)	32.5	230	78	62.2	340	43	2.94%
Ga (g/t)	10	15	1.7	4.4	-	-	-
Hg (g/t)	9.0	0.2	22	63.3	-	14.5	-
Te (g/t)	1.7	1.4	3.4	51.8	-	-	-

(A) Oxidation smelting of 4-Level ore

The average operating conditions for a test run treating 4-Level ore were as given in Table 4 while analyses of materials were as set out in Tables 5 to 11.

Table 4 – Average operating conditions for a run treating 4-Level ore

Feed rate - ore	200 kg/h
Feed moisture	1%
Limestone addition	50 kg/h
Coal feed rate	20 kg/h
Average temperature	1319°C
Average lance air flow rate	309.6 Nm^3/h
Average lance oxygen flow rate	27.1 Nm^3/h
Oxygen content of lance air	Approximately 27%
Average oil flow rate	23.72 l/h

Table 5 – Ore composition during the run (%)

Zn	Pb	Fe	S	SiO_2	MgO	Al_2O_3	C	CaO	K
14.0	10.4	16.5	24.5	24.5	0.58	4.40	1.06	0.116	1.70

Table 6 – Average analysis of the slag during the course of the trial (%)

Zn	Pb	Fe	S	SiO_2	Al_2O_3	CaO	MgO
4.2	0.2	18.3	2.4	33.0	7.2	18.8	3.6

Table 7 – Fume composition at the end of the trial

Zn	35.7%	BaO	40 ppm	Sb	297 ppm
Pb	32.0%	CaO	706 ppm	Cr	20 ppm
Ag	191 ppm	As	4110 ppm	Sn	150 ppm
Fe	0.21%	Cu	306 ppm	Tl	104 ppm
S	5.49%	F	850 ppm	Ge	116 ppm
SiO_2	0.20%	Cl	600 ppm	Se	-
Al_2O_3	0.05%	Cd	889 ppm	Ni	39 ppm
K	0.53%	Na	97 ppm	Ga	-
C	0.35%	Co	4 ppm	Hg	33 ppm
MgO	0.02%	Mn	7 ppm	Bi	-

Table 8 – Limestone composition during the run

Zn	Pb	Fe	S	SiO$_2$	MgO	Al$_2$O$_3$	C	CaO	K
22 ppm	38 ppm	0.08 %	150 ppm	0.6%	0.50 %	0.20 %	-	54.0 %	0.08 %

Table 9 – Ultimate analysis of coal

Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur
86.0%	4.5%	1.9%	6.5%	1.0%

Table 10 - Proximate analysis of coal

Moisture	Ash	Volatiles	Fixed carbon	Gross calorific value
1%(air dried)	13.4%	22.1%	63.5%	30.5 MJ/kg

Table 11 - Analysis of ash in coal

	%		%
SiO$_2$	67.4	TiO$_2$	1.81
Al$_2$O$_3$	26.4	MN$_3$O$_4$	0.01
Fe$_2$O$_3$	1.96	SO$_3$	0.09
CaO	0.54	P$_2$O$_5$	0.49
MgO	0.15	BaO	0.09
Na$_2$O	0.11	SrO	0.12
K$_2$O	0.44	ZnO	0.06

5

(B) Reduction smelting of slag from 4-Level ore

The average operating conditions for a test run during smelting of the slag were as set out in Table 12. The composition of the coal was the same as detailed in Tables 9 to 11, while other analyses of materials were as set out in Tables 13 to 15.

Difficulties may be encountered when attempting a mass balance on the data of Table 15 through analytical error, sampling error, and hold-up of same elements in the fume collection system. This hold-up can result in some material from previous smelting trials reporting to the fume of the current trial, and some of the material from the current trial reporting to the fume of future trials.

Table 12 – Conditions during reduction smelting of slag from 4-Level ore

Feed rate - slag	260 kg/h
Feed moisture	1%
Limestone addition	0 kg/h
Coal feed rate	22 kg/h
Average temperature	1308°C
Average lance air flow rate	235.3 Nm^3/h
Average lance oxygen flow rate	46.1 Nm^3/h
Oxygen content of lance air	34%
Average oil flow rate	46.7 l/h
Average ambient temperature	22.4°C

Table 13 – Feed slag composition (%)

Zn	Pb	Fe	S	SiO_2	Al_2O_3	CaO	MgO
9.6	< 0.01	20.5	4.7	31.0	6.2	18.0	2.0

Table 14 – Average analysis of the slag during the course of the reduction trial

Zn	Pb	Fe	S	SiO_2	Al_2O_3	CaO	MgO
1.08%	<0.01%	23.1%	1.69%	33.84%	7.2%	18.1%	4.0%

Table 15 – Fume composition at the end of the reduction trial

Zn	62.7%	MgO	0.02%	Co	7 ppm
Pb	11.2%	BaO	59 ppm	Mn	4.5 ppm
Ag	328 ppm	CaO	533 ppm	Sb	379 ppm
Fe	0.13%	As	1644 ppm	Cr	32 ppm
S	2.37%	Cu	375 ppm	Sn	174 ppm
SiO_2	0.25%	F	684 ppm	Tl	46 ppm
Al_2O_3	0.05%	Cl	830 ppm	Ge	97 ppm
K	0.69%	Cd	234 ppm	Ni	41 ppm
C	0.83%	Na	97 ppm	Hg	11 ppm

(C) Oxidation smelting of bulk concentrate

The average operating conditions for a test run during smelting of bulk concentrate were as set out in Table 16. The composition of the coal was the same
5   as detailed in Tables 9 to 11, while other analyses of materials were as set out in Tables 17 to 19.

Table 16 – Conditions during smelting of bulk concentrate

Feed rate - bulk concentrate	145 kg/h
Feed moisture	1%
Limestone addition	10 kg/h
Coal feed rate	20 kg/h
Average temperature	1323°C
Average lance air flow rate	252.3 Nm^3/h
Average lance oxygen flow rate	20.7 Nm^3/h
Oxygen content of lance air	Approximately 27%
Average oil flow rate	14.3 l/h
Average ambient temperature	17.5°C

10

Table 17 – Bulk concentrate composition (%)

Zn	Pb	Fe	S	SiO$_2$	MgO	Al$_2$O$_3$	C	CaO	K
25.25	17.25	13.5	27.0	8.2	0.25	1.87	0.93	0.06	0.84

Table 18 – Average slag analysis during oxidation smelting of bulk concentrate(%)

Zn	Pb	Fe	S	SiO$_2$	Al$_2$O$_3$	CaO	MgO
9.05	0.36	28.15	2.7	26.0	6.9	9.75	3.10

Table 19 – Analysis of fume from oxidation smelting of bulk concentrate

Zn	39.2%	MgO	0.02%	Mn	1.4 ppm
Pb	29.1%	BaO	32 ppm	Sb	213 ppm
Ag	251 ppm	CaO	90 ppm	Cr	17 ppm
Fe	0.07%	As	2350 ppm	Tl	44 ppm
S	5.32%	Cu	183 ppm	Ge	28 ppm
SiO$_2$	0.10%	F	50 ppm	Ni	3.6 ppm
Al$_2$O$_3$	< 0.05%	Cl	< 200 ppm	Hg	2.6 ppm
K	0.28%	Cd	776 ppm		
C	0.04%	Na	40 ppm		

(D) Oxidation smelting of high-grade ore

5   The average operating conditions for a test run during the smelting of high-grade ore were as set out in Table 20. The composition of the coal again was as detailed in Tables 9 to 11, while other analyses were as set out in Tables 21 to 23.

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Table 20 – Operating conditions during the smelting of high-grade ore

Feed rate-ore	105 kg/h
Feed moisture	1%
Limestone addition	5 kg/h
Coal feed rate	15 kg/h
Average temperature	1297°C
Average lance air flow rate	377 Nm^3/h
Average lance oxygen flow rate	0 Nm^3/h
Oxygen content of lance air	Approximately 21%
Average natural gas flow rate	20 Nm^3/h
Average ambient temperature	18.9°C

Table 21 – Feed ore composition (%)

Zn	Pb	Fe	S	SiO$_2$	MgO	Al$_2$O$_3$	CaO
42.0	4.0	9.0	30.0	8.0	<0.1	3.5	<0.1

Table 22 – Slag composition during run (%)

Zn	Pb	Fe	S	SiO$_2$	Al$_2$O$_3$	CaO	MgO
13.9	0.1	21.0	3.1	26.7	8.7	11.6	2.9

Table 23 – Fume composition during oxidation smelting of high-grade ore run

Zn	67.4%	BaO	51 ppm	Mn	4.8 ppm
Pb	9.25%	CaO	108 ppm	Sb	214 ppm
Ag	157 ppm	As	990 ppm	Cr	206 ppm
Fe	0.13%	Cu	75 ppm	Sn	89 ppm
S	2.18%	F	130 ppm	Tl	80 ppm
SiO$_2$	0.17%	Cl	200 ppm	Ge	30 ppm
Al$_2$O$_3$	0.05%	Cd	1350 ppm	Ni	15 ppm
K	0.14%	Na	40 ppm	Hg	4.1 ppm
MgO	0.01%	Co	1.1 ppm		

5

EXAMPLE 2

Fume separation tests were conducted to investigate individual processing steps, and to follow through the process sequence and provide data for optimization of the processing steps. Major steps which were separately investigated were:-

5
- *Prewash* - to remove sulphate and halides.
- *Leaching* - to selectively dissolve and separate zinc from lead and silver.
- *Iron Purification* - to separate elements such as arsenic and germanium from zinc.
- *Zinc Dust Cementation* - to separate elements more electropositive than

10   zinc, such as lead, copper, cadmium, nickel and cobalt.
- *Steam Stripping* - to separate zinc from solution as a basic carbonate.
- *Calcination* - to convert the basic zinc carbonate to a high grade zinc oxide.

The testwork was conducted using fume produced during the oxidation and reduction smelting of 4 - Level ore, as detailed in EXAMPLE 1. The fume was mixed

15   in a ratio of two parts oxidation fume and one part reduction fume. A typical analysis of the resulting mixture is given in Table 24.

Table 24 - A typical analysis of the fume used in hydrometallurgical trials.

Zn	44.1%	Ag	242 ppm	Ca	210 ppm
Pb	28.6%	Ge	70 ppm	Mg	120 ppm
T/S	4.97%	Ni	20 ppm	K	680 ppm
Fe	0.066%	Co	35 ppm	Cl	300 ppm
As	0.274%	Tl	90 ppm·	F	34 ppm
Cd	0.075%	Se	<2 ppm	Si	470 ppm
Cu	0.018%	Hg	6 ppm		

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(A) Prewash

The oxidation smelting of sulphide ores generates sulphur dioxide. Under typical fume collection conditions, SO_2 combines with lead and other oxide fumes to form sulphates. Such sulphate formation was predominantly associated with lead

25   when it is present in the fume. Most of the sulphur contained in the fume collected during the smelting trials was present as sulphate. The amount of sulphur present as

sulphate in the fume from which the analysis given in Table 24 was derived, was 4.88% out of the total of sulphur content of 4.97%. Calculations and x-ray diffraction suggest that virtually all the lead was present as sulphate.

In the pilot fuming trials the fume collection temperature was lower than expected in practice, where a lower degree of lead sulphation might be expected. However, even in the fume produced from commercial plants there would be sufficient sulphate present to accumulate in the AAC circuit. It has been shown earlier testwork that this will reduce the capacity of the solution to dissolve zinc by association with free ammonia, and will co-precipitate with the basic zinc carbonate, being retained within and degrading the calcined zinc oxide product. The zinc content of the product zinc oxide can be reduced from 80% to 72% as a result of the presence of sulphate, even with controlled removal from recirculating leach solution by lime treatment, which must follow the precipitation stage.

To avoid these difficulties the fume was prewashed with a sodium carbonate solution to remove sulphate prior to AAC extraction of zinc. Three stoichiometric ratios of carbonate to sulphate were examined (1.1, 1.2 and 1.4 times the stoichiometric amount calculated for removal of all the sulphate) and sulphate removal was efficient in all cases within an allowed reaction time of 30 minutes. Sulphate removal at 1.1 x stoichiometric was marginally less efficient at 91% compared with 95% at the higher levels. Zinc and lead extractions into the soda ash treatment solution were less than 0.01% based on solution analyses and are therefore considered negligible.

The prewash also served to separate halides. The indications from fume and washed fume analyses indicated 75 to 80% chlorine removal and 85 to 90% fluorine removal.

Tests using an ammonium carbonate prewash showed a significantly lower sulphate removal efficiency by about 30%, and up to 3.5% of the zinc was extracted. Adjustment of pH to the same level as for soda ash prewash resulted in high zinc extractions and was clearly not appropriate. Consequently the soda ash prewash is the preferred method.

After the pre-wash, the fume (with precipitated carbonate) was removed by filtration and washed in dilute soda ash solution.

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(B) Leaching

After the pre-wash, the fume was leached in AAC solution of 120 g/l NH_3 and 100 g/l CO_2. A first series of tests showed the solution could dissolve 140 g/l Zn.

It was found that the temperature of the leach should be maintained below a
level where there could be significant loss of ammonia which is taken as around 65 °C. Initial tests showed a temperature rise during leaching of 15 to 17 °C for dissolution of 110 g/l Zn. Hence the starting temperature of the leach solution was taken as 45 °C.

Average analyses of prewashed fume and leach residues, together with
calculated extractions for four leaching tests at the above optimum conditions, are given in Table 25.

Table 25 - Average resulte of leaching fume with AAC solutions

Element	Prewashed Fume %	Average Leach Residue %	Average Extraction %
Zn	48.3	0.97	99.2
Pb	30.2	74.68	0.51
S	0.51	0.145	88.6
Fe	0.072	0.156	12.8
As	0.32	0.066	91.7
Cd	0.082	0.037	82.0
Cu	0.029	0.036	27.5
Ge	0.0075	0.0009	95.4
Ag	0.029	0.061	14.8
Mg	0.0013	0.002	39.6
K	0.075	0.077	95.8
Cl	0.029	0.012	83.3
F	0.0034	0.0010	87.8
Tl	0.0058	0.0018	87.3
Ni	0.0023	0.0026	55.2
Co	0.0004	0.00045	52.2
Si	0.0511	0.015	87.8

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The first series of tests also showed similar zinc and lead extractions at 99.2% and 0.4% respectively, giving a high degree of separation of the two major components.

Based on solution analyses and considering the reliability of analyses, there was no significant difference in the proportion of zinc extracted for leaching times of between 10 minutes and 40 minutes.   Hence zinc extraction from fume was found to be rapid, and not influenced by normal practical residence times.

Based on the analysis of the fume and the leach residue, silver extraction was around 15% which will mean some loss from the production of lead bullion derived from leach residue. However analyses of the leach solution and calcined zinc oxide product suggested negligible dissolution of silver.   If in fact a significant level of dissolution of silver did occur it was able to be recovered in leach residue from the electrolytic zinc operation.

Copper extraction was found to be low at around 27.5%. This was believed to be due the fact that the copper was present in carryover slag or feed material from fuming operations and may be as a sulphide in a matte phase of the slag rather than as a copper oxide.

Arsenic and germanium extractions were quite high, as was thallium.   No attempt was made to minimise these by recovery of the fume at a high temperature. The other surprising result was the high extraction of silicon, but this possibly resulted from the presence of zinc silicates.

Selenium, mercury and manganese were generally below analytical detection levels in the particular materials examined.

Halides were efficiently extracted during the leaching operation which may imply that improved filter cake washing of the pretreated fume could improve the separation of halides at that point.

It is proposed that the leach residue is reduced in a rotary furnace to yield a lead bullion. Table 26 shows the calculated levels of arsenic, silver and copper in that lead bullion.

Table 26 - Calculated impurity levels in lead bullion.

Element	Expected %	Specification %
As	0.09	0.001 max
As	0.086	0.001 max
Cu	0.051	0.001 max

The standard lead refining operations of copper drossing, softening and desilvering could be used to produce high grade lead.   Other elements are likely to have been predominantly contained in reduction furnace slag (eg. iron, nickel, cobalt, germanium) or in fume (eg. cadmium).

(C) Ferrous sulphate addition

The objective of this procedure was to add iron in a soluble form (ferrous sulphate), to oxidize and precipitate it as ferric hydroxide, whereby impurities such as arsenic and germanium would coprecipitate with the iron.   This is a   common purification procedure from acid sulphate solutions, but is unknown in application to AAC solutions.

Table 27 gives the results of the first and second series ferrous sulphate addition tests.

Table 27 - Results of ferrous sulphate addition.

	Zn g/l	Fe added mg/l	Final Fe mg/l	As mg/l	Ge mg/l	Fe:As ratio in solids	Fe:Ge ratio in solids
Series 1							
Start soln.	113		35	761	21		
Run 1		2,000	425	488	1.6	5.9	83
Run 2		4,000	489	661	9.9	35.5	320
Run 3		6,000	192	134	<0.5	9.3	285
Run 4		10,000	454	143	<0.5	15.5	467
Series 2							
Start soln.	126		47	774	19		
Run 1	123	1,200	448	674	14	8.0	160
Run2	131	1,200	486	693	14	9.4	152

To reduce Ge and As to 1 mg/l in acid sulphate solutions by this method may require Fe:Ge ratios of around 200 to 300:1 and Fe:As ratios of between 10 and 15:1. Although the above results are variable, it would appear that performance is comparable with these generalized ratios, and it is clearly an appropriate impurity removal technique provided sufficient iron is added. Using the general ratios it might be expected that between 8 and 12 g/l of iron must be added to remove 770 mg/l As and 20 mg/l Ge. This is largely dictated by arsenic removal. If this quantity of iron is added as ferrous sulphate then up to 20 g/l SO_4 will also be added, which is excessive, and counters the objectives of the pretreatment step.

Although this is an effective method of As and Ge removal it may be preferable to add the iron in a different form or to conduct the iron purification within the following electrolytic zinc plant circuit.

(D) Zinc dust addition

The second method of impurity removal to separate elements more electropositive than zinc was by cementation using zinc powder. In particular this was applicable to the removal of lead, cadmium, copper, nickel, cobalt and thallium. There were clearly optimum reaction times to avoid reversion or re-solution, and this was evident for lead and cadmium. The comparative results for various tests at 1.5 g/l zinc dust addition, with and without pretreatment and at residence times of 30 and 180 minutes are given in Table 28.

Table 28 - Results of zinc dust addition

Time mins.	Pb mg/l	Pb recov. %	Cu mg/l	Cu recov %	Cd mg/l	Cd recov. %	Tl mg/l	Tl recov. %
Series 1 (No prewash) Series 2 (With prewash, Sulphur at 2.03 g/l)								
30	13	97	2	86	5	96	0.2	98.3
180	48	87		100	2	98	0.14	98.8
Series 2 repeat (With prewash, Sulphur at 0.6 g/l)								
30	45	89	1.2	98.6	7	95.6	0.36	96.4
180	4	99	1.2	98.6	62	61.3	0.27	97.3

Table 28 - Continued

Series 2 repeat (Without prewash, Sulphur at 12 g/l)

30	24	94.3	0.1	99.9	8.7	94.6	0.69	93.1
180	<1	100	0.1	99.9	2.3	98.6		

Series 2. Three stage zinc dust addition with prior ferrous sulphate addition

30	53	86	2.0	85.7	5	96.2	0.2	98.3
180	48	87.4					0.14	98.8

Series 2   Three stage repeat without prior ferrous sulphate addition.

30			7.5	91.1	15	90.6	0.85	91.5
180	0.2	100	1.2	98.6	0.6	99.6	0.05	99.5

High levels of removal of these elements was possible, although the results were somewhat variable.   There was some indication of reversion, but it would appear that a relatively simple zinc dust procedure may be suitable.   There did not appear to be any merit in a three stage zinc dust addition.

Zinc dust cementation had minimal impact on the level of arsenic in solution, but had a variable effect on the removal of germanium, reducing concentration down to 1.5 mg/l in one case.   Thus, cementation may be a useful additional step to ensure low levels of germanium in the final zinc oxide product.

(E) Steam stripping

Zinc was precipitated from solution as a basic zinc carbonate by removal of ammonia and carbon dioxide from solution by steam stripping. In practice this would be conducted in a continuous multistage system (4 or 5 stages).   However in testwork, this step was conducted using a batch approach, in which steam was continuously passed through a fixed volume of pregnant solution until all the zinc has been precipitated.   Two steam rates were used at 10% and 20% of the solution volume in litres as kg/h of injected steam.   Solution samples taken at various times were analysed and provide useful information on equilibrium solution compositions.

Solution composition data from the literature, such as the above-reference article by Wendt, is indicated in Table 29.

Table 29 - AAC solution composition.

NH$_3$ g/l	CO$_2$ g/l	Zn g/l
10	7	2
20	15	21
30	32	47
60	47	72
80	62	95
100	78	120
120	93	145

The above indicates a molar ratio of NH$_3$: Zn of 3.2 and a CO$_2$: Zn molar ratio of close to 1.0, except at low levels of zinc where NH$_3$ and CO$_2$ levels are higher than these ratios would suggest.   Solution samples taken from our tests in which sulphate levels are low, closely conform to the above table.   If sulphate is present the NH$_3$:Zn correlation is displaced to higher than expected levels of NH$_3$. This is accounted for by association of free ammonia with the sulphate and was apparent in our tests.

Tests on the steam required to strip ammonia and carbon dioxide from solution and precipitate zinc to a residual concentration suggest that about 600 g of steam per litre of solution is required to separate 120 g of zinc in batch laboratory procedure using small scale equipment. For a practical multistage system it is expected that the steam rate should be significantly below the batch rate by a factor of at least 2.   This would suggest a steam requirement of around 2.5 g/g of zinc recovered.

It is clearly feasible to recover zinc to final solution levels of less than 0.5 g/l which represents a first pass recovery from leach solution of better than 99.5%. Much of the residual zinc will be recycled and is not lost from the process. Overall recoveries from stripping can exceed 99.8%.

The deportment of other elements over the leach - steam strip operations may be shown by the percentage recoveries from prewashed fume to calcined zinc oxide product as given in Table 30.

Table 30 - Recoveries to calcined zinc oxide product (%)

Element	Recovery without zinc dust	Recovery with zinc dust	Element	Recovery without zinc dust	Recovery with zinc dust
Zn	99.8	99.7	K	3.6	0.06
Pb	0.47	0.06	Cl	10.7	10.5
As	78.5	71.7	F	7.3	1.8
Ge	95	0	Tl	51.2	0.6
Cu	26.6	1.5	Ni	48.5	5.3
Ge	90.8	89.2	Co	61.9	30.4
Si	71.7	60.5			

Some of the data is not particularly consistent but does indicate quite reasonable separation efficiencies particularly with the inclusion of zinc dust cementation.

(F) Calcination

Tests showed minimal difference in zinc oxide purity at calcination temperature between 300, 450 and 600 °C. The zinc oxide analyses for the same material were 71.4%, 73.5% and 73.8% respectively. Consequently it was considered that calcination at 300 °C was adequate. In the case of initial tests, the residual sulphate was high at 2.7% (8.1% SO_4) due to the absence of pretreatment.

For later 2 tests, washed basic zinc carbonate averaging around 58.5% Zn was calcined at 300 °C for two hours to give a consistent product at 78.4% zinc and 0.25% C (1.25% CO_3). The sulphur content averaged 0.08% (0.24% SO_4), giving a total accounted analysis as follows:

ZnO   =   95.70 %

$ZnCO_3$ =   2.61 %

$ZnSO_4$ =   0.40 %

Total accounted =   98.71 %

Final zinc oxide product can be broadly grouped into material produced with and without purification by zinc cementation. Table 31 gives average analyses for

these two groups produced from the later calcination tests, including pretreatment for sulphate removal:

Table 31 - Analyses of calcined zinc oxide product (%)

Element	Without Zn dust treatment	With Zn dust treatment
Zn	78.1	78.8
Pb	0.23	0.015
S	0.11	0.058
Fe	0.376	0.41
As	0.38	0.38
Cd	0.067	0.0002
Cu	0.0062	0.0005
Ge	0.01	0.0078
Ag	ND	ND
Mg	ND	ND
K	0.0074	ND
Se	0.0005	0.0005
Hg	ND	ND
Cl	0.005	0.005
F	0.0003	0.0004
Tl	0.0045	0.0001
N	0.018	0.017
C	0.25	0.25
Ni	0.0018	0.0002
Co	0.0003	<0.0001
Si	0.053	0.058
Mn	0.0014	0.0013

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The zinc oxide product was clearly high grade with adequate control of most elements of concern to subsequent metallurgical operations, with the possible exception of arsenic and germanium. If the zinc oxide was required as feed to a dedicated and simplified electrowinning zinc plant without solution

10   purification, then additional measures to control these elements would be

necessary. Higher temperature collection of smelter fume will enhance the separation of arsenic from fume. Iron precipitation is also likely to be effective for control of these elements as well as silica, but will require optimization of iron addition and precipitation procedures. Alternatively neutral leaching of the zinc oxide with some iron addition in the electrolytic zinc circuit, should also be effective in control of these impurities and may be preferable since it is a well established procedure.

If zinc oxide is to be used in a conventional electrolytic zinc plant equipped with zinc dust purification and iron precipitation facilities, the impurity levels will be quite manageable for oxide produced without zinc dust treatment.

It can be argued that any electrowinning plant should at least include a zinc purification stage to act as a safeguard against accidental impurity input and to enable poor solution quality to be recovered. If this is the case, then it would seem preferable to carry out all such cementation purification at the electrolytic plant where the zinc dust is readily available and the bulk of the contained zinc is automatically recycled.

Halides are the primary elements of concern in the use of fume product in a conventional electrolytic zinc plant, and these are adequately controlled by the fume separation process, meeting target levels of 50 ppm for chlorine and 5 ppm for fluorine. Soluble elements such as magnesium, potassium and manganese are also well controlled by this process.

Finally, it is to be understood that various alterations, modifications and/or additions may be introduced into the constructions and arrangements of parts previously described without departing from the spirit or ambit of the invention.

CLAIMS:

1.   A process for the recovery of zinc values from feed comprising zinc sulphide-containing raw material, wherein the process includes the steps of:

(a)   smelting the raw material in the presence of a carbonaceous reductant to substantially reduce the zinc sulphide to metallic zinc, and to vaporize the zinc, thereby producing furnace gases containing zinc vapour and sulphur dioxide;

(b)   contacting the furnace gases produced in step (a) with free-oxygen containing gas to oxidize the zinc metal and to produce zinc oxide rich crude fume in said furnace gases;

(c)   separating the crude fume from the furnace gases and collecting the crude fume;

(d)   mixing the collected crude fume with concentrated aqueous ammonia/carbon dioxide solution having a stoichiometric excess of ammonia to produce a zinc-bearing leach liquor and to leave a solids residue and separating said leach liquor from the residue;

(e)   stripping ammonia from the separated leach liquor to precipitate basic zinc carbonate and to leave a stripped leach liquor and separating the stripped leach liquor from the basic zinc carbonate; and

(f)   calcining the basic zinc carbonate to produce a purified zinc oxide product.

2.   A process according to claim 1, wherein the raw material is selected from zinc sulphide ore and zinc sulphide concentrate.

3.   A process according to claim 1 or claim 2, wherein step (a) is conducted in furnace selected from a flash smelting shaft furnace, a high temperature flame reactor, a shaft furnace, a kiln furnace, a slag bath reactor adapted for lance injection and a slag bath reactor adapted for tuyere injection.

4.   A process according to claim 1 or claim 2, wherein the raw material is smelted in at least one top-submerged lancing reactor containing a molten slag bath, and the slag is agitated by injecting free-oxygen containing gas into the slag.

5.   A process according to claim 4, wherein step (a) is conducted in two stages in which the first stage is more oxidizing whereby sulphur is substantially eliminated from the raw material as sulphur dioxide to leave zinc oxide taken up by the slag, and the second stage is more reducing whereby the zinc oxide in the slag is reduced to metallic zinc and vaporized.

6.   A process according to any one of claims 1 to 5, wherein said raw material includes lead and silver values which, after steps (a) and (b), report in the crude fume; and wherein the filtering of step (d) separates said leach liquor from lead and silver containing solids.

7.   A process according to any one of claims 1 to 6, wherein the zinc oxide rich crude fume contains metal values present therein at least in part as sulphate; and wherein, between steps (c) and (d), the process further includes the steps of washing the crude fume with an aqueous carbonate wash solution whereby metal values present as sulphate are precipitated as carbonate to leave a wash solution containing sulphate ions, and separating from the sulphate bearing wash solution a solids mixture which is substantially free of sulphate and which comprises the washed fume product and the precipitated carbonate.

8.   A process according to claim 7, wherein the crude fume is washed with a wash solution comprising a solution of a carbonate selected from the group consisting of alkali metal and ammonium carbonates.

9.   A process according to claim 8, wherein said wash solution comprises a solution of sodium carbonate.

10.   A process according to any one of claims 1 to 9, wherein the reductant is selected from coal, coke, coke breeze, natural gas, LPG and fuel oil.

11.   A process according to claim 10, wherein the reductant is selected from lump coal and particulate coal.

12.   A process according to any one of claims 1 to 11, wherein part of the reductant is comsumed as a fuel in step (a) to provide at least part of the energy requirement for smelting the raw material, and wherein free oxygen-containing gas is supplied to the furnace at a rate sufficient for the smelting, combustion of the fuel and oxidation to produce said crude fume.

13.   A process according to any one of claims 1 to 12 wherein the raw material contains minerals of base metals additional to zinc, and wherein the smelting of step (a) and the contacting of step (b) are such that at least one of the base metals reports in the crude fume product as a compound selected from oxide, sulphate, a volatile compound derived from the minerals, and mixtures thereof.

14.   A process according to claim 13, wherein the at least one base metal includes at least one of antimony, arsenic, cadmium, copper, germanium, lead, nickel and selenium.

15.   A process according to claim 14, wherein the at least one base metal includes at least one of a group including antimony, arsenic, germanium and selenium, and wherein the process further includes, after the mixing but before the separating of step (d), treating the zinc-bearing leach liquor by iron sulphate addition and by aeration by injected air, whereby ferric hydroxide is precipitated with co-precipitation of the at least one metal of said group and, in step (d), separating the leach liquor from a mixture of the residue and precipitates.

16.   A process according to claim 14 or claim 15, wherein the at least one base metal includes at least one of a group including cadmium, cobalt, copper, lead and nickel, and wherein the process further includes, between steps (d) and (e), adding zinc dust to the separated leach liquor whereby the at least one metal of the group including cadmium, cobalt, copper, lead and nickel is precipitated by a cementration reaction, and the leach liquor is filtered to remove the precipitate therefrom.

17.   A process according to any one of claims 13 to 16, wherein the at least one base metal includes at least one of a group including antimony, arsenic, germanium and selenium and wherein, in step (e), the crude fume is collected at a temperature at which the at least one metal of the group is present as the vapour of the base metal or of a compound thereof, whereby collection of the at least one base metal with the crude fume is substantially prevented.

18.   A process according to any one of claims 1 to 17, wherein the process further includes the step of digesting the zinc oxide product in sulphuric acid solution of a circuit of a conventional electrolytic process for the production of metallic zinc, whereby the zinc oxide product comprises at least part of conventional zinc source material for the electrolytic process.

19.   A process according to any one of claims 1 to 17, wherein the process further includes the step of digesting the zinc oxide product, in at least one stage, in spent electrolyte of a circuit for the production of metallic zinc by an electrolytic process, whereby to provide a neutral zinc sulphate solution for which the zinc oxide product comprises substantially the sole input of zinc to the electrolytic process.

20.   A process according to claim 19, wherein the neutral zinc sulphate solution as produced is separated from any solids materials therein and then passed directly to electrolytic cells for the production of metallic zinc.

21.   A process according to claim 19, wherein the process further includes adding ferrous iron in soluble form to the zinc sulphate solution, neutralizing and oxidising the resultant solution with air to precipitate hydrated ferric oxide whereby to co-precipitate minor impurity residuals therein, separating the resultant solids and passing the clear solution to further stages in the electrolytic process.

22.   A process according to claim 19, wherein the process further includes treating the neutral zinc sulphate solution with zinc dust whereby to precipitate

minor impurity residuals therein, filtering the treated solution and then passing the filtered solution directly to electrolytic cells for the production of metallic zinc.
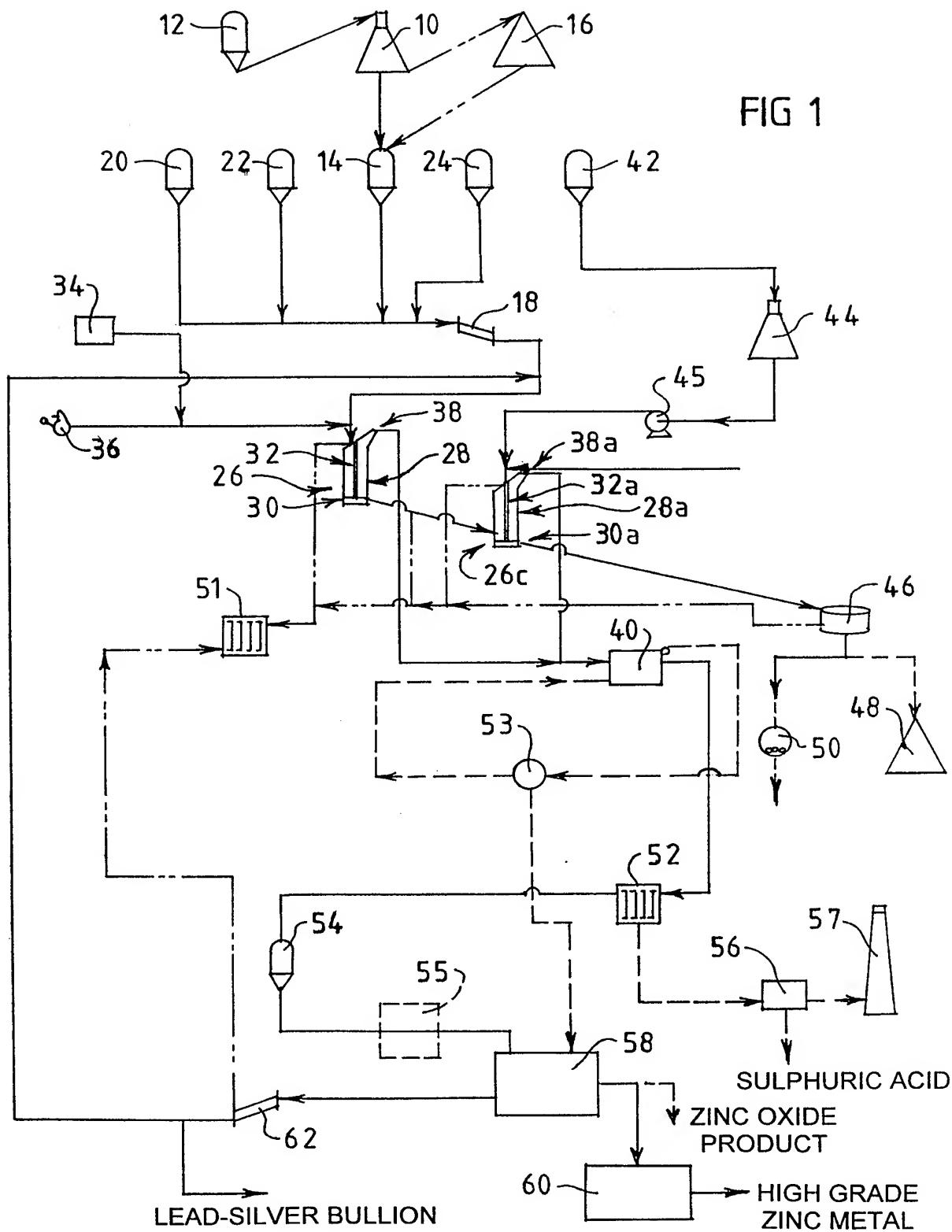
23. A process according to any one of claims 19 to 22, wherein the process further includes separating a minor portion of said zinc sulphate solution, treating said minor portion to precipitate basic zinc sulphate, separating the basic zinc sulphate to leave a barren liquor and recycling the basic zinc sulphate to the step of digesting the zinc oxide in sulphuric acid solution, whereby to control the build-up of soluble halides and other soluble impurities in said circuit.

24. A process according to any one of claims 1 to 23, wherein the process further includes the step of agglomerating the zinc oxide product into a substantially dust free form.

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FIG 1

LEAD-SILVER BULLION

SULPHURIC ACID

ZINC OXIDE
PRODUCT

HIGH GRADE
ZINC METAL

LIMESTONE

SODA ASH

54

55

55a

55c

55i

55h

55f

55d

55e

55g

GYPSUM

86

H_2O

CO_2

72

75a

94

75

75b

74

70

76

Zn DUST

82

84a

84b

78a

78

80

85

62

88

Cd,Cu,Ni
CEMENT

LEAD-SILVER BULLION

90

90a

92

SLAG

DISCARD

FIG 2

60

HIGH GRADE
ZINC METAL

ZINC OXIDE
PRODUCT
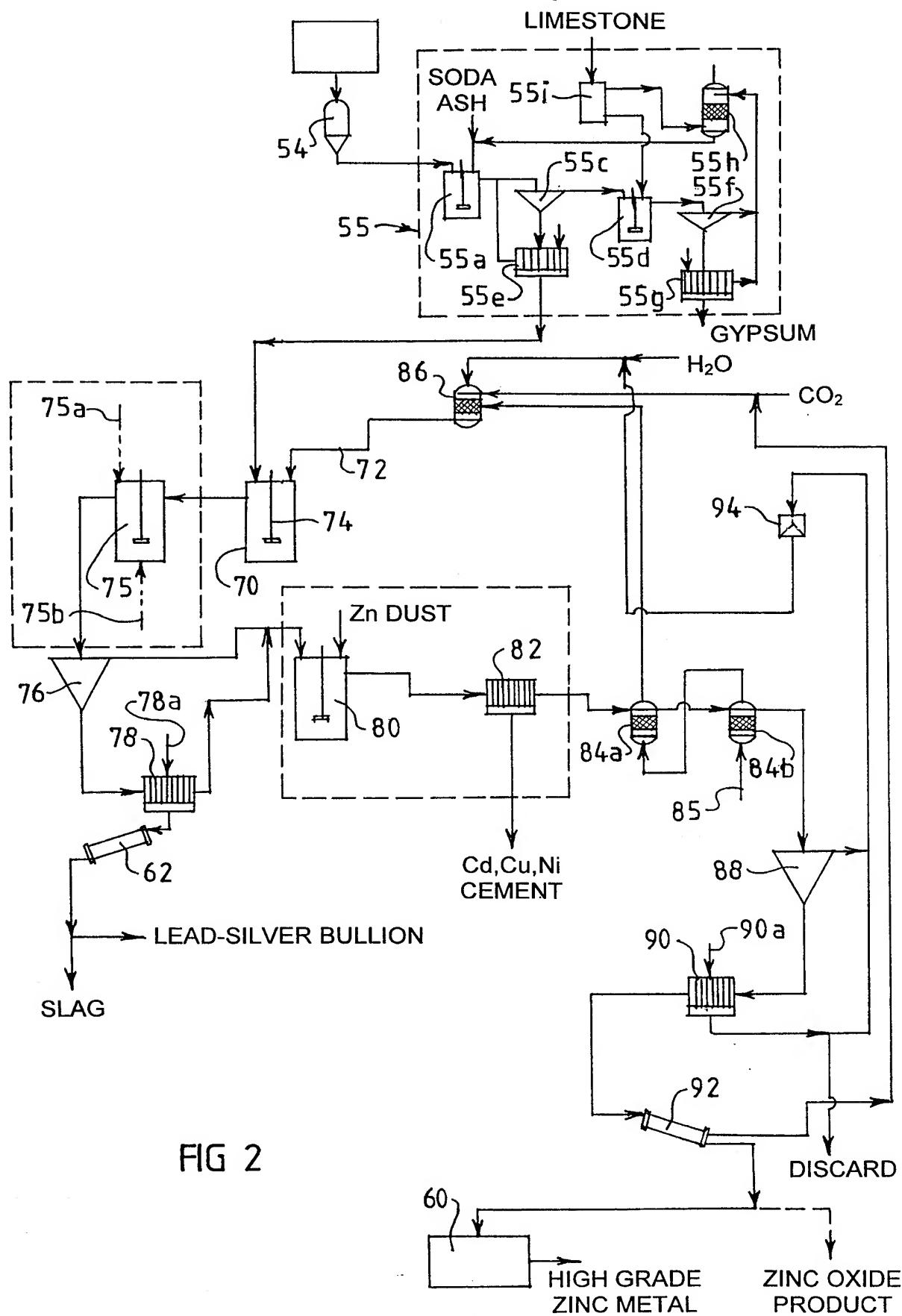
3/3

FIG 3

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: C22B 19/04, 19/08, 19/34, 19/36

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC Int. Cl[6] C22B 19/04, 19/08, 19/34, 19/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
ORBIT (DERWENT ON-LINE): (C22B OR C01G) AND (ZINC OR ZN) AND [(FUME: OR DISTILL: OR VAPO:) OR ((NH3 OR NH4 OR AMMONI:) AND (CO2 OR CARBON()DIOXIDE OR CARBONATE))] period 1975-98

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4169725 A (MAKIPIRTTI) 2 October 1979 See claim 1, examples	1-24
Y	AU 20280/83 B (564479) (VSESOJUZNY NAUCHNO-ISSLEDOVATELSKY GORNO-METALLURGICHESKY INSTITUT TSVETNYKH METALLOV) 26 April 1985 See claim 1, examples	1-24
Y	WO 91/08317 (MOUNT ISA MINES LIMITED) 13 June 1991 See claim 1, examples	1-24

[X] Further documents are listed in the continuation of Box C	[X] See patent family annex

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 March 1998	09 APR 1998

Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929	Authorized officer **G.J. BROXAM** Telephone No.: (02) 6283 2133
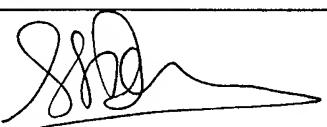
C (Continuation)	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 88/01654 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 10 March 1988. See abstract, examples	1-24
Y	US 4071357 A (PETERS) 31 January 1978 See abstract, examples	1-24
Y	GB 2238528 A (ECOMETAL S.r.L.) 5 June 1991 See abstract, examples	1-24
Y	US 5538532 A (KEEGEL) 23 July 1996 See abstract, examples	1-24
Y	CA 1200701 A (COMINCO LTD.) 18 February 1986 See claim 1	7

INTERNATIONAL SEARCH REPORT
Information on patent family members

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member						
AU	20280/83	DE	3341154	IN	161943			
WO	91/08317	AU	68934/91					
GB	2238528	CA	2025161	DE	4033232	FR	2653450	
		IT	1236233					
WO	88/01654	AU	79186/87					

END OF ANNEX